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SYNTHESES AND REARRANGEMENTS OF ORGANOALKALI COMPOUNDS

A THESIS

Presented to

the Faculty of the Graduate Division

by

Yao-Ming Cheng

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SYNTHESES AND REARRANGEMENTS OF ORGANOALKALI COMPOUNDS

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Chairman

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SUMMARY

The purpose of this research was to study the syntheses and possible rearrangements of some organoalkali compounds using lithium metal or cesium alloys as the source of the alkali metal cation.

In the first part of this research, the syntheses of simple alkyl anions were investigated under various conditions via the reaction of a simple alkyl halide or a dialkylmercury compound with a binary cesium-potassium alloy (m.p. -41°) consisting of 22 percent of cesium and 78 percent potassium (by weight) or a ternary alloy (m.p. -79.2°) consisting of 73 percent cesium, 24 percent potassium, and 3 percent sodium. The products from these reactions were reacted with solid carbon dioxide to convert the organoalkali compounds to carboxylic acids. These acids were then converted to the corresponding methyl esters by reacting with diazomethane and the esters analyzed by quantitative vapor-phase chromatography. Some of the hydrocarbons which accompanied the acids were analyzed by the same technique.

The reaction of 1-chlorobutane with the binary cesium alloy for a short time (from three to 20 minutes) in tetrahydrofuran or diethyl ether at -36 to -43° gave 0.6 to 5.5 percent of butyl anion as demonstrated by the isolation of valeric acid. In order to test the effect of temperature, the ternary cesium alloy was reacted with 1-chlorobutane in tetrahydrofuran or diethyl ether at temperatures from -73 to -95° for time intervals from two to 15 minutes. The yields of butyl anion ranged from 0.4 to 19.0 percent with the maximum yield of 19 percent in diethyl ether. The same reaction in dimethyl ether, over the temperature range ca. -60 to -107° gave

from 0.2 to 13.3 percent yield of butyl anion. The yield of butyl anion was found to decrease with increasing reaction time.

The reaction of 1-chloroheptane with the ternary cesium alloy in tetrahydrofuran at -65° in 17 minutes followed by carbonation gave 1.5 percent of octanoic acid, 24 percent heptane, 14 percent of 1-heptene, and 29 percent unreacted chloride. A similar reaction in trimethylamine gave 7.5 percent of octanoic acid, 1.8 percent heptane, 0.5 percent 1-heptene, 5.0 percent octane, and 0.6 percent unreacted chloride. The low yields of products were presumably due to solvent distillation of the hydrocarbon products.

In view of the fact that under basic conditions a primary alkyl halide undergoes dehydrohalogenation to give an olefin which, in turn, may react with the excess alkali metal or with carbanion to give undesired side products, a better starting material was desirable. The choice for this purpose was di-n-butylmercury. The cleavage of di-n-butylmercury with the ternary cesium alloy for one hour in tetrahydrofuran at -67° gave up to 34 percent yield of butyl anion. When this cleavage reaction was carried out in diethyl ether at -70°, a 37 percent yield of butyl anion was obtained in 15 minutes and the yield decreased to 11.0 percent after an additional 30 minutes of reaction; in the meantime the yield of the unreacted di-n-butylmercury recovered was found to decrease from 44 percent to 2.2 percent. The same reaction was repeated in dimethyl ether at -70° and the desired carbanion was obtained in only 0.25 percent yield after 15 minutes of reaction. The yield changed slightly (to 0.20 percent) after an additional 30 minutes of reaction. An attempt was made to test the solubility of butyl anion by nmr spectroscopic analysis of a reaction

solution from the cleavage of di-n-butylmercury in diethyl ether at both Dry Ice-acetone and liquid nitrogen temperatures. This experiment failed to show any absorption upfield from tetramethylsilane. Thus, it is concluded that simple primary carbanions are short-lived (the half life of butyl anion in THF is about eight minutes at -70°) and apparently not very soluble in diethyl ether.

In the second part of this research, 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) was reacted with various alkali metals and the products were carbonated. Both the acidic and neutral products were analyzed by vapor-phase chromatography and some of the neutral products were also analyzed by nuclear magnetic resonance spectroscopy. The reaction of 1-chloro-2-methyl-2-phenylpropane with lithium in tetrahydrofuran at -65° for four hours followed by carbonation gave 71 percent of 3-methyl-3-phenylbutanoic acid, 3.3 percent 2,2-dimethyl-3-phenylpropanoic acid, 6.4 percent t-butylbenzene, 2.9 percent i-butylbenzene, and 13 percent of unreacted neophyl chloride. Both i-butylbenzene and 2,2-dimethyl-3-phenylpropanoic acid result from the rearranged organolithium compound, 1,1-dimethyl-2-phenylethyllithium, the product of a 1,2-shift of the phenyl group in some phase of the reaction. The average proportion of 2,2-dimethyl-3-phenylpropanoic acid in the mixture of acids from five similar runs was 5.3 ± 0.5 percent. The proportion of this acid of rearranged structure was found to decrease from 6.4 percent during preparation at -60° to 5.5 percent after four hours at -70° and to 3.9 percent after an additional four hours at -70°. An increase in reaction temperature from -65° to -40° for two hours decreased the proportion of 2,2-dimethyl-3-phenylpropanoic acid a similar amount but had little effect on the yield of 3-methyl-3-

phenylbutanoic acid. An increase in temperature to 4° for four hours resulted in a negligible yield of 2,2-dimethyl-3-phenylpropanoic acid and a greatly reduced yield of 3-methyl-3-phenylputanoic acid with approximately corresponding increases in yields of t-butylbenzene and i-butylbenzene, respectively. Thus, the data indicate that the rearranged organolithium compound is formed along with the expected neophyllithium during the reaction of neophyl chloride with lithium. The results are explained on the basis that neophyl chloride reacts with lithium metal by a one-electron transfer process to give neophyl radical which in part is free enough from the metal to undergo a 1,2-migration of phenyl; reduction of the radicals with lithium then gives the observed organolithium products.

Neophyllithium prepared in tetrahydrofuran at -65° has been found to be moderately stable photochemically. The irradiation of a neophyllithium solution (prepared in 86 percent yield in tetrahydrofuran) with a 450 watt Hanovia lamp at -74° for 13½ hours followed by carbonation resulted in a slight decrease in yields of acidic product. The composition of the acidic material (97 percent unrearranged and 3 percent rearranged) from the photochemical reaction was essentially identical with that of the acidic material (96.5 percent unrearranged and 3.5 percent rearranged) from a similar procedure without irradiation.

The presence of a large excess of N,N,N',N'-tetramethylethylenediamine (TMEDA) in the solution of neophyllithium in tetrahydrofuran at -20° resulted in a decrease in yield of both the rearranged and unrearranged acids. Attempts to promote the rearrangement of neophyllithium by alkyl halides and iodine have produced some higher molecular weight compounds in place of the desired products.

The cleavage of neophyllithium with the ternary cesium alloy in tetrahydrofuran at -65° gave, after carbonation, 80 percent of a crude acidic product which contained 81 percent 3-methyl-3-phenylbutanoic acid, 5.0 percent 2,2-dimethyl3-phenylpropanoic acid, and three unidentified compounds in the volatile fraction. When the same cleavage reaction was carried out at -10° the yields of both the rearranged and unrearranged acids were found to decrease and the yields of the corresponding hydrocarbons, t-butylbenzene and i-butylbenzene, were found to double those obtained at -65°.

The reaction of neophyl chloride with potassium in refluxing tetrahydrofuran, followed by carbonation, gave only 6.7 percent of acidic products which contained three normal molecular weight acids in an overall yield of 0.53 percent. None of these acids was identified as 3-methyl-3-phenylbutanoic, 2-methyl-2-phenylbutanoic, 2,2-dimethyl-3-phenylpropanoic, o-, m-, or p-t-butylbenzoic acid. From the neutral material was obtained 64 percent of t-butylbenzene and 6.2 percent of i-butylbenzene.

The reaction of neophyl chloride with the binary cesium alloy (at -40° and -60°) and with the ternary cesium alloy (at -65°) in tetrahydrofuran, followed by carbonation, gave up to 3 percent (based on the halide used) of 2-methyl-2-phenylbutanoic acid among others. This acid results from the carbanion corresponding to methyl migration and has not been observed in the lithium reaction. When the reaction was carried out in diethyl ether, 3-methyl-3-phenylbutanoic acid obtained in 0.86 percent yield (based on the halide used) constituted 43 percent of the total volatile acidic products. 2-Methyl-2-phenylbutanoic acid turned out to be a minor product (constituted 0.91 percent of the volatile acidic mixture).

In the third part of this research, both 1-chloro-2-p-biphenylethane and 1-chloro-2-p-biphenylylethane-1,1-d_2 were reacted with alkali metals and the products were carbonated. The techniques which were used in the second part of this research were also used here for product analyses.

In a single run, the reaction of 1-chloro-2-phenylethane with lithium in tetrahydrofuran has been found to give, after carbonation, 69 percent of 3-phenylpropanoic acid. The reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with lithium in tetrahydrofuran at -70° gave up to 69 percent yield of 2-p-biphenylylethyllithium-1,1-d_2 containing less than 10 percent of the rearranged compound 2-p-biphenylylethyllithium-2,2-d_2. The 2-p-biphenylylethyllithium-1,1-d_2 has been found to be fairly stable at 0° for three hours, where the acidic product obtained in 46 percent yield was found to be predominantly the unrearranged acid, 3-p-biphenylylpropanoic acid-2,2-d_2, contaminated by less than 10 percent of the acid of rearranged structure, 3-p-biphenylylpropanoic acid-3,3-d_2. When the reaction was prolonged to nine hours or longer at 0°, only 17 percent of the organolithium compound survived and the acidic product resulting from the carbonation was found to be mainly the unrearranged compound; less than 2 percent of rearranged acid was detected. The neutral product from these experiments was found to yield 50 percent (based on the halide used) of p-biphenylylethane-d_2, which contained mainly p-biphenylylethane-2,2-d_2 with a small amount (ca. 6 percent) of p-biphenylylethane-1,1-d_2. Thus 2-p-biphenylylethyllithium prepared at -70° undergoes little rearrangement if any and it is moderately stable even at 0°; there is also no significant rearrangement at the higher temperature.

1-Chloro-2-p-biphenylylethane-1,1-d_2, however, has been found to

react with Cs-K-Na alloy in tetrahydrofuran at -65° to give 25 percent of p-biphenylylethane-d_2 containing 78 percent of p-biphenylylethane-2,2-d_2 and 22 percent of p-biphenylylethane-1,1-d_2. The reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with cesium at refluxing tetrahydrofuran has been found to give 19 percent of p-biphenylylethane-d_2 containing 48 percent of p-biphenylylethane-2,2-d_2 and 52 percent of p-biphenylylethane-1,1-d_2. When the same chloride was reacted with potassium at refluxing tetrahydrofuran, p-biphenylylethane-d_2 obtained in ca. 25 percent yield was found to contain 47 percent of p-biphenylylethane-2,2-d_2 and 53 percent of p-biphenylylethane-1,1-d_2. Thus, 1-chloro-2-p-biphenylylethane-1,1-d_2 reacts with either cesium or potassium at the boiling point of tetrahydrofuran to give a complete rearrangement of the carbanion initially formed; the reaction with the ternary cesium alloy at -65° gives some rearrangement which is incomplete but more than that obtained in the corresponding organolithium reaction.

1-Chloro-2-p-biphenylylethane-1,1-d_2 reacted with potassium in the presence of t-BuOD in refluxing tetrahydrofuran to give a mixture containing 39 percent saturated hydrocarbons, 53 percent p-biphenylylethene-2,2-d_2, together with some 8 percent of an unidentified compound. The saturated hydrocarbons consisted of 50 percent d_3, 16 percent d_2, 29 percent d_4, 4 percent d_5, and 1 percent d_6 compounds. The d_3 fraction was found to be mainly (> 90 percent) unrearranged p-biphenylylethane-2,2,2-d_3 which resulted predominantly from the reaction of the initially formed 2-p-biphenylylethyl-1,1-d_2 anion with t-BuOD. This observation serves to support the conclusion that rearrangement occurs in the 2-p-biphenylylethyl-1,1-d_2 anion. This anion generated from the reaction of the corresponding

chloride with both potassium and cesium in refluxing tetrahydrofuran (in the absence of t-BuOH) undergoes rearrangement apparently through a bridged transition state to give an equilibrium mixture of both rearranged and unrearranged carbanions. These carbanions were protonated readily by the solvent yielding the corresponding hydrocarbons.

It is concluded that the small amount of rearrangement observed in the preparation of 2-p-biphenylylethyllithium-1,1-d_2 apparently results from the free radical process as has been found in the second part of this work. However, the reaction of the same halide with cesium or potassium undergoes a rearrangement predominantly by a carbanion process.

CHAPTER I

INTRODUCTION

The purpose of this research was to study the syntheses and possible rearrangements of some organoalkali compounds.

While some organolithium reagents, such as phenylithium and butyllithium, are commercially available, primary alkylsodium compounds[1] and alkylpotassium compounds[2,3] are difficultly available and have been studied only in hydrocarbon solvents. Even though ethylcesium in diethylzinc solution was reported as early as in 1926 by Grosse,[4] primary organocesium compounds as a group have not been widely explored.

The most common method for the synthesis of organoalkali compounds is the reaction of alkyl halides or alkylmercury with alkali metals.[5] Morton's sodium sand method[1] and a similar method using potassium sand have been widely employed for the syntheses of organosodium and organopotassium compounds in hydrocarbon media. Both sodium and potassium reagents have been used as metalating agents[6-11] and polymerization cata-

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(1) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, J. Am. Chem. Soc., 72, 3785 (1950).

(2) R. A. Finnegan, Tet. Lets., 26, 1303 (1962).

(3) R. N. Meals, J. Org. Chem., 9, 211 (1944).

(4) V. Grosse, Ber., 59, 2646 (1926).

(5) R. A. Finnegan, Tet. Lets., 7, 429 (1963).

(6) R. A. Benkeser, A. E. Trevillyan, and M. Hooz, J. Am. Chem. Soc., 84, 4971 (1962).

lysts.[12-14] However metalations using these reagents have been found to take place rather slowly conceivably due to the low solubility of these reagents in hydrocarbon solvents. As possible new metalating agents, alkylcesium compounds in ethereal media seem to be a good choice.

The organoalkali compounds prepared from the reactions of 2-chloro-1,1,1-triphenylethane with sodium,[15] lithium, potassium, and sodium-potassium alloy[16] have been found to undergo rearrangement due to 1,2-migration of a phenyl group. A 1,2-shift of a biphenylyl group has also been observed in the reaction of 2-chloro-1-m-biphenylyl-1,1-bis (p-biphenylyl) ethane with lithium.[17] In these cases the rearranged organoalkali compounds are thermodynamically more stable than the original organoalkali compounds.

$$Ar_3CCH_2M \xrightarrow{\sim Ar} Ar_2\underset{M}{C}CH_2Ar$$

(7) A. A. Morton, J. T. Massengale, and M. L. Brown, ibid., 67, 1620 (1945).

(8) R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, ibid., 85, 3984 (1963).

(9) C. D. Broaddus, J. Org. Chem., 29, 2689 (1964).

(10) C. D. Broaddus and D. L. Muck, J. Am. Chem. Soc., 89, 6533 (1967).

(11) A. A. Morton and E. J. Lanpher, J. Org. Chem., 23, 1636 (1938).

(12) A. A. Morton and R. L. Letsinger, J. Am. Chem. Soc., 69, 172 (1947).

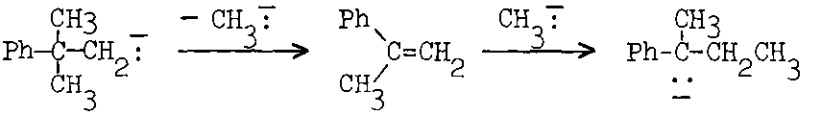
(13) D. Braun and M. Herner, J. Polymer Sci., 51, 52 (1961).

(14) D. Braun and W. Kern, ibid., 197 (1965).

(15) E. Grovenstein, Jr., J. Am. Chem. Soc., 79, 4985 (1958).

(16) E. Grovenstein, Jr. and L. P. Williams, Jr., ibid., 83, 412 (1961).

1-Chloro-2-methyl-2-phenylpropane (neophyl chloride), which contains both methyl and phenyl groups at β-carbon, is a good model for the study of rearrangements of an organoalkali compound involving 1,2-migration. If an organoalkali compound derived from neophyl chloride undergoes carbanion rearrangement due to a 1,2-phenyl-migration, the product will be a thermodynamically less stable tertiary carbanion. However, if such rearrangement occurs by a free radical process,[18] the rearranged tertiary radical will be more stable than the starting primary radical.[18a] On the contrary, if one of the methyl groups migrates, the rearranged carbanion should be thermodynamically more stable than the original primary carbanion. But such a migration for a thermal reaction violates orbital symmetry requirements for a concerted intramolecular rearrangement.[19] Nevertheless the rearrangement might occur by an elimination-readdition mechanism



or by a photochemical process.

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(17) E. Grovenstein, Jr. and G. Wentworth, ibid., 89, 2348 (1967).

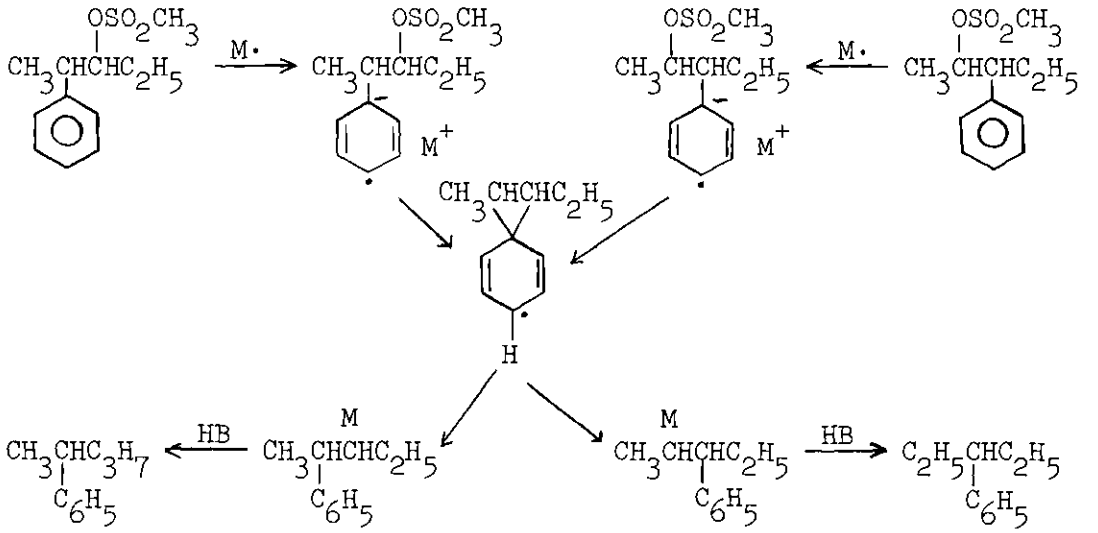
(18) W. H. Urry and M. S. Kharasch, ibid., 66, 1438 (1944).

(18a) C. Rüchardt and H. Trautwein, Ber., 95, 1197 (1962).

(19) N. F. Phelan, H. H. Jaffe', and M. Orchin, J. Chem. Education, 44, No. 11, 626 (1967); H. E. Zimmerman and A. Zweig, J. Am. Chem. Soc., 83, 1196 (1961).

When Williams studied the synthesis of 1-lithio-2-methyl-2-phenylpropane, he was able to prepare the desired organolithium compound in 66 percent yield.[20] He did not report any organolithium compounds resulting from methyl or phenyl migration; however, he observed a small amount of hydrocarbon which could result from the protonation of the rearranged organolithium compound.

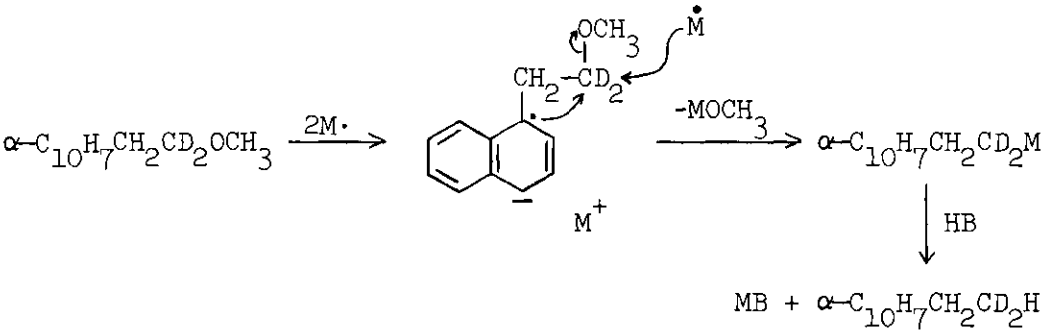
Cram and Dalton[21] have studied the reaction of potassium with threo-2-phenyl-3-pentyl methanesulfonate in dimethoxyethane and sodium with threo-3-phenyl-2-pentyl methanesulfonate in liquid ammonia and they obtained good yields of hydrocarbons containing mainly the unrearranged product together with a small amount (6 percent for the former and 3 percent for the latter) of rearranged products. They proposed the following mechanism to account for the rearrangement:



(20) L. P. Williams, Jr., Ph.D. Thesis, Georgia Institute of Technology, p. 16 (1962).

(21) D. J. Cram and C. K. Dalton, J. Am. Chem. Soc., 85, 1268 (1963).

But, the reduction of both 1,1-dideuterio-2-(1-naphthyl)-ethyl methanesulfonate and 1,1-dideuterio-1-methoxy-2-(1-naphthyl)-ethane with potassium in dimethoxyethane yielded only the unrearranged 1-ethylnaphthalene deuterated in the methyl group and the following mechanism was postulated for the reduction of the methoxy compound:



Organoalkali compounds, especially organopotassium compounds, are notorious for their instability even at room temperature, hence, it is desirable that syntheses be attempted at low temperatures in suitable solvents. In this work, both a liquid binary alkali metal alloy, which was previously employed in this laboratory[22] and a liquid ternany alkali metal alloy[23] (m.p. -79.2°) consisting of 73 percent cesium, 24 percent potassium, and 3 percent sodium (by weight) will be used to react with organic halides and occasionally organomercury compounds.

In the first part of this research, the syntheses of simple alkyl anions were performed by reacting 1-chlorobutane, 1-chloroheptane, and di-n-butylmercury with cesium alloys in various solvents at low temperatures.

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(22) Y. M. Cheng, M.S. Thesis, Georgia Institute of Technology, p. 53 (1967).

(23) F. Tepper, J. King, and J. Greer, "The Alkali Metals," Chem. Soc., London, 1967, p. 23.

The products were allowed to react with solid carbon dioxide to convert the organoalkali compounds to carboxylic acids. The acids were analyzed as methyl esters by vapor-phase chromatography. The hydrocarbon products from the reaction of 1-chloroheptane were also analyzed by the same technique.

In the second part of this work, the synthesis of neophyllithium from the reaction of neophyl chloride with lithium metal was reinvestigated. The activation of an organolithium compound by complexing with a ditertiary amine has been demonstrated by Langer in his studies of BuLi-N,N,N',N'-tetramethylethylenediamine(TMEDA) catalyzed polymerization and metalation.[24] He has concluded that strong complex between chelating agent and lithium has caused an increase in the ionic character of the Li-C bond. The possibility of photochemically and thermally induced rearrangement was studied. Neophyllithium was also allowed to react with cesium alloy, alkyl halides, iodine, and TMEDA in order to see whether there was any enhancement in rearrangements. Neophyl chloride was reacted with cesium alloys and potassium; the carbonation products were analyzed by vapor-phase chromatography. The hydrocarbon products were also analyzed by nuclear magnetic resonance spectroscopy.

In the third part of this research, both 1-chloro-2-p-biphenylylethane and 1-chloro-2-p-biphenylylethane-1,1-d_2 were synthesized using 4-acetylbiphenyl as the starting material. The halides were reacted with lithium, potassium, cesium, and cesium-potassium-sodium alloy in tetrahydrofuran and the products carbonated. The carbonation products were analyzed by vapor-phase chromatography and nuclear magnetic resonance spectroscopy.

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(24) A. W. Langer, Jr., Trans. N.Y. Acad. Sci., 27, 741 (1965).

CHAPTER II

REAGENTS AND SOLVENTS

4-Acetylbiphenyl

Aldrich grade 4-acetylbiphenyl (m.p. 112-8°) was recrystallized from ethanol to give a sample, m.p. 119-20°.

Benzene

Industrial grade (thiophene free) benzene was stored over sodium wire.

t-Butyl Alcohol

Baker reagent grade t-butyl alcohol was redistilled from over molten potassium at 81° through a 60 cm vacuum jacketed column packed with glass helices.

t-Butyl Alcohol-OD

Merck Sharp & Dohme of Canada Ltd. grade t-butyl alcohol-OD was used without further purification (nmr analysis shows 98.8 atom % D).

o-t-Butylbenzoic Acid

A sample prepared by L. P. Williams, Jr., m.p. 67-9°, was used without further purification.[25]

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(25) L. P. Williams, Jr., Ph.D. Thesis, Georgia Institute of Technology, p. 54 (1962).

m-t-Butylbenzoic Acid

A sample prepared by L. P. Williams, Jr.,[26] m.p. 127-8°, was used without further purification.

p-t-Butylbenzoic Acid

A sample prepared by L. P. Williams,[27] m.p. 164.0-5.0°, was used without further purification.

i-Butylbenzene

Chemical Samples Co., 99.7 percent pure, i-butylbenzene was used.

s-Butylbenzene

Baker grade s-butylbenzene was used.

t-Butylbenzene

Aldrich unspecified grade t-butylbenzene was found to be VPC pure.

Carbon Disulfide

Baker reagent grade carbon disulfide was used without further purification.

Carbon Tetrachloride

Baker reagent grade carbon tetrachloride was used without further purification.

Cesium

MSA Research Corp., 99.9 percent purity minimum, cesium was used.

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(26) L. P. Williams, Jr., ibid., p. 56 (1962).

(27) L. P. Williams, Jr., ibid., p. 50 (1962).

1-Chlorobutane

Columbia grade 1-chlorobutane was redistilled at 77-8° through a 60 cm vacuum jacketed column packed with glass helices.

1-Chloroheptane

Aldrich grade 1-chloroheptane was redistilled at 115° and 15 cm pressure through the same column used above.

1-Chloro-2-methyl-2-phenylpropane

A sample prepared by L. P. Williams, Jr.,[26] was redistilled at 86° under 5 mm pressure through a Nester-Faust annular Teflon spinning band column.

Decalin

Eastman technical grade decalin was extracted with conc. sulfuric acid and then distilled at 102-4° under 70 mm pressure.

Deuteroacetone

A sample of incompletely labeled deuteroacetone (96.7 percent CD_3COCD_3) from Organic Stockroom of the School of Chemistry, Georgia Tech, was used.

Deuterochloroform

Volk grade chloroform-d was used without further purification.

Dibutylmercury

Eastman white label grade dibutylmercury was redistilled at 96-8° under 15 mm pressure through the same column used for 1-chlorobutane.

Diethyl Ether

Baker reagent grade diethyl ether was used without further purification.

Dimethyl Ether

A cylinder of dimethyl ether from Air Products and Chemicals was used.

Ethyl Alcohol

Commercial grade absolute alcohol was used without further purification.

Heptane

Philips Petroleum Co., 99 percent minimum, heptane was dried over sodium wire.

1-Heptene

Chemical Samples Co., 99 percent pure, 1-heptene was used without further purification.

cis-2-Heptene

Chemical Samples Co., 95 percent, cis-2-heptene was used without further purification.

trans-2-Heptene

Chemical Samples Co., 99 percent, trans-2-heptene was used without further purification.

cis-3-Heptene

Chemical Samples Co., 95-7 percent, cis-3-heptene was used without further purification.

trans-3-Heptene

Chemical Samples Co., 99 percent, trans-3-heptene was used without further purification.

Iodomethane

Eastman white label grade iodomethane was used without further purification.

Lithium

Lithium Corporation of America, 0.05 percent sodium max., and Foote Mineral Co., 1 percent sodium, lithium wires were used.

Lithium Aluminum Deuteride

Stohler Isotope Chemicals, 99 percent D, lithium aluminum deuteride was used without further purification.

Lithium Aluminum Hydride

City Chemical Corp., 95 percent minimum, lithium aluminum hydride (grey chunk) was ground up and used without further purification.

Methallyl Chloride

Baker purified grade methallyl chloride was redistilled at 69-70.5° through the same column used for 1-chlorobutane.

Methanol

Commercial grade methanol was purified by treatment with magnesium at reflux and then distilled at 64°.

2-Methyl-2-phenylbutanoic Acid

A sample prepared by L. P. Williams, Jr.,[27] m.p. 57-8°, was used without further purification.

3-Methyl-3-phenylbutanoic Acid

A sample prepared by L. P. Williams, Jr.,[28] m.p. 56-8°, was used without further purification.

Morpholine

Aldrich puriss grade morpholine was used without further purification.

Octanoic Acid

Aldrich grade octanoic acid was used without further purification.

n-Pentane

Philips Petroleum Co., 99 percent minimum pure, n-pentane was used without further purification.

Potassium

Baker reagent grade potassium was used.

Pyridine

Fisher, ACS Certified grade, pyridine was dried over potassium

(28) L. P. Williams, Jr., ibid., p. 49 (1962).

hydroxide pellets.

Sodium

Baker reagent grade sodium was used.

Sulfur

Baker N. F. grade sulfur was used.

Tetrahydrofuran

Baker reagent grade tetrahydrofuran was stored over sodium wire before use.

N,N,N',N'-Tetramethylethylenediamine

Eastman white label grade N,N,N'N'-tetramethylethylenediamine was redistilled at 120-1°.

Thionyl Chloride

Baker purified grade thionyl chloride was used without further purification.

Toluene

Baker reagent grade toluene was stored over sodium wire before use.

Tributyl Amine

Eastman white label grade tributyl amine was redistilled at 190-2°.

Valeric Acid

Baker grade valeric acid, b.p. 186-7°, was used without further purification.

CHAPTER III

GENERAL PROCEDURE OF REACTIONS AND INSTRUMENTAL ANALYSES OF PRODUCTS

General Procedure

For reactions with lithium and potassium, a three-necked, 500-ml, Morton flask equipped with a high-speed Morton stirrer was used. The apparatus was flame-dried with a stream of dry nitrogen sweeping through the flask, and then cooled to room temperature under an atmosphere of nitrogen. Solvent was then distilled from over sodium aluminum hydride or lithium aluminum hydride directly into the reaction vessel unless otherwise specified. The same procedures for drying the apparatus and solvent purification were used for reactions of cesium and cesium alloys; however, these reactions were conducted inside a glove-box filled with a nitrogen atmosphere using a four-necked, 500-ml, modified Morton flask equipped with a short modified Morton stirrer.

Instrumental Analyses

All nmr spectra were obtained on a Varian Associates Model A-60 spectrometer using tetramethylsilane as an external or internal standard depending respectively on whether the relative intensities of each absorption were needed or only the chemical shifts of each kind of hydrogen were important. Carbon tetrachloride was used as solvent except in the case of carbinols where deuterochloroform or deuteroacetone was used.

Infrared spectra were taken on a Perkin-Elmer Grating Infrared

Spectrophotometer model 237B using carbon tetrachloride (for chlorides) and carbon disulfide (for carbinols) as solvents with a 0.2 mm sodium chloride cell and were calibrated with the 6.238 μ band of polystyrene film.

VPC analyses of the reaction products were accomplished by using either F & M Research Chromatograph Model 810 (F & M) or Perkin-Elmer Model 881 Gas Chromatograph (P-E). The columns used are given in Table 1 and the typical operating conditions are given in Table 2.

Table 1. Columns for VPC Analyses of Reaction Products

Column Number	Liquid Phase (% Coating)	Solid Phase*	(mesh)	Length (Outside Diameter)
I	Diethylene glycol succinate (10%)	Chromosorb G	(60-80)	6' ($\frac{1}{4}$")
II	Apiezon L (10%)	Chromosorb P	(60-80)	6' ($\frac{1}{4}$")
III	Silicone gum rubber, GE, SE-30 (10%)	Chromosorb G	(60-80)	6' ($\frac{1}{4}$")
IV	Polyphenyl Ether (15%)	Chromosorb W	(80-100)	6' ($\frac{1}{4}$")
V	Apiezon L (10%)	Chromosorb W	(80-100)	12' ($\frac{1}{8}$")
VI	Silicone gum rubber, GE, SE-30 (5%)	Chromosorb G	(100-120)	12' ($\frac{1}{8}$")

*Solid phases had been acid-washed and treated with dimethyldichlorosilane.

Acid from the reaction of 1-chlorobutane and dibutylmercury with

cesium alloys was analyzed as methyl ester by adding a known weight of ethylbenzene as internal standard to an aliquot of the ether solution of the ester; a measured volume of this solution was injected into the VPC. Measured volumes of standard solutions of ethylbenzene and methyl valerate were also injected separately as standards for calibration. The analyses of products from other reactions were all done by dissolving an aliquot of a sample in a known volume of solvent and then injecting a measured volume of this solution. Measured volumes of the authentic sample solutions of known concentration were injected separately for calibrations. The calculations were based on the assumption that the area to weight ratio of a compound in an unknown mixture was identical to the area to weight ratio of that same compound in an authentic sample solution. The yields of products were then expressed in weight and/or percentage; percentage yields so determined are referred to as "absolute" yields. If only the approximate relative composition of the volatile products was determined, only VPC area percent or area ratios were used; percentage yields so determined are called "relative" yields.

Table 2. Typical Operating Conditions for VPC Analyses

Material Analyzed	Column Number	Instrument	Oven Temp.	Carrier Gas	
				Flow (mm)	Pres. (psig.)
Methyl Valerate	I	F & M	90°	15	40
Octane	II	F & M	90°	20	40
Dibutylmercury	II	F & M	160°	20	30
Methyl Octanoate	I	F & M	100°	21	40
Heptane and Heptenes	IV	P-E	65°	12	40
1-Chloroheptane	IV	P-E	125°	12	40
Tetradecane	IV	P-E	172°	12	40
Photochemistry of Neophyllithium					
Methyl Esters	I	F & M	143°	23	50
Neutral Products	III	F & M	200°	18	40
Stability and Rearrangement of Neophyllithium					
Esters from Runs 1 and 2	I	F & M	174°	20	48
Reaction of Neophyl Chloride with Cs Alloys					
Neutral (Runs 1 to 3)	III	F & M	182°	18.5	50
Other Neophyl Chloride Reactions					
Esters	V	P-E	190°	24	60
Butylbenzenes	V	P-E	140°	20	60
Neophyl Chloride	V	P-E	163°	20	60
Reactions of 1-Chloro-2-p-biphenylylethane					
Esters	VI	P-E	172°	26	60
Hydrocarbons	VI	P-E	153°	26	60

CHAPTER IV

EXPERIMENTAL DETAILS*

Synthesis of 1-Chloro-2-p-Biphenylylethane

p-Biphenylylacetic Acid

The title compound was prepared following the procedure of Schwenk and Papa.[29] In a typical run, starting with 100 g (0.510 mole) of 4-acetylbiphenyl there was obtained 102 g (0.481 mole, 94.3 percent yield) of crude p-biphenylylacetic acid, m.p. 155-8°. Recrystallization from benzene gave 68.2 g (0.322 mole, 63.1 percent), m.p. 160-162°. In four other runs an overall yield of 42 percent of the purified acid was obtained.

2-p-Biphenylylethanol

The reduction of p-biphenylylacetic acid was first carried out in a 500 ml Morton flask fitted with a high-speed stirrer by adding 5.22 g (0.0246 mole) of p-biphenylylacetic acid in 50 ml tetrahydrofuran to a suspension of 1.66 g (0.0440 mole) of lithium aluminum hydride in 250 ml freshly distilled tetrahydrofuran under reflux dropwise over a period of 25 minutes. The mixture was stirred at reflux for another three hours. Then ethylacetate (50 ml) was added to decompose unreacted lithium aluminum hydride. The reaction mixture was then poured into 250 ml of a 1:1 mixture of dil. HCl and ice, extracted with four 100 ml portions of ether. The

*For infrared spectra of compounds, see Appendix A.

(29) E. Schwenk and D. Papa, J. Org. Chem., 11, 798 (1946).

ethereal extracts were combined, washed with three 100 ml portions of 5 percent $NaHCO_3$ and two 100 ml portions of water, dried over anhydrous $MgSO_4$, and filtered. After removing the solvents there was obtained 5.22 grams of solid material, m.p. 96-102°. One recrystallization from ethanol gave 3.68 g of crude carbinol, m.p. 90-92° (premelts at 87°). A second recrystallization from both ethanol and carbon tetrachloride gave 2.15 g, m.p. 94-5°, 0.443 g, m.p. 93-5°, and 0.0875 g, m.p. 91-3°. The reported[30] melting point of 2-p-biphenylylethanol is 93°.

The desired carbinol was successfully prepared when excess lithium aluminum hydride was used. In a typical run, a solution of 51.0 g (0.240 ml) of p-biphenylylacetic acid in 450 ml of tetrahydrofuran was added dropwise over a period of 140 minutes under an atmosphere of nitrogen to a suspension of 27.8 g (0.733 mole) of lithium aluminum hydride in 1500 ml of tetrahydrofuran. The mixture was then stirred at reflux for an additional six hours. To the flask was next added cautiously some water (ca. 200 ml) to decompose excess $LiAlH_4$. A usual work up produced 48.9 g (0.246 mole, 102 percent yield based on p-biphenylylacetic acid used) of crude product, m.p. 93-5°. One recrystallization from carbon tetrachloride gave 36.3 g of white crystals, m.p. 95-6°, and 5.01 g of a less pure material, m.p. 94.5-6°. The nmr spectrum [a multiplet centered at 2.61 τ (9.26 H), aromatic hydrogens; a triplet centered at 6.14 τ (2.00 H, J = 6.5 cps), methylene group adjacent to OH; another triplet centered at 7.13 τ (2.00 H, J = 6.5 cps), methylene group adjacent to aromatic ring; and a singlet at 8.45 τ (1.16 H), OH group] indicated that this compound was essentially pure 2-p-biphenylylethanol.

(30) J. Colonge and P. Rochas, Bull. Soc. Chim. France, 825 (1948).

In another two runs, a scale of from 20 g to 55 g of acid was reduced with excess $LiAlH_4$ (1 RCO_2H : 3 $LiAlH_4$) in a similar manner giving quantitative yields of the desired carbinol, m.p. 92-96°. One recrystallization from CCl_4 gave sufficiently pure 2-p-biphenylylethanol, m.p. 95-96°. The nmr spectrum was identical with that given above.

1-Chloro-2-p-biphenylylethane

The conversion of 2-p-biphenylylethanol into 1-chloro-2-p-biphenylylethane was first attempted by following a modified procedure of Roberts.[31] In a 200 ml, three-necked, round-bottomed flask fitted with a condenser and dropping funnel was placed 4.96 g (0.025 mole) of 2-p-biphenylylethanol, 100 ml anhydrous ether, and 2.90 g of triethylamine. The mixture was stirred with a magnetic stirrer at ice-bath temperature (0-5°) and then thionyl chloride (3.23 g, 0.0271 mole) was added at such a rate that the temperature did not exceed 8° over a period of 15 minutes. The first portion of thionyl chloride added caused the precipitation of white solid material. The mixture was stirred at boiling point of ether for three and one-half hours and then poured into 300 ml of crushed ice. Ether extraction yielded some light brown oily product, which was recrystallized from ethanol giving 0.156 g of solid material, m.p. 100-103°, and 2.39 g of oily material. An attempted recrystallization of this oily material from pentane was unsuccessful. The above 0.156 g of solid material was again recrystallized from ethanol to give 0.116 g, m.p. 106-7°. A sample of this material was analyzed for C, H contents.

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(31) M. C. Caserio, W. H. Graham, and J. D. Roberts, Tetrahedron, Vol. 11, p. 171 (1960).

Anal.* Found: C, 75.65, 75.44; H, 5.78, 5.71. Calcd. for $C_{28}H_{26}SO_3$ [(p-$PhC_6H_4CH_2CH_2)_2SO_3$]: C, 76.00; H, 5.92.

In the next attempt, to a mixture of 10.0 g (0.0506 mole) of 2-p-biphenylylethanol and 10.3 g (0.0557 mole) of tri-n-butylamine at ice-bath temperature was added slowly 6.65 g (0.0559 mole) of thionyl chloride and the mixture was then refluxed for three hours. A usual work up yielded 10.6 g, m.p. 77-94°. One recrystallization from ethanol gave 1.01 g, m.p. 105-6°, 1.01 g, m.p. 70-92°, 0.450 g, m.p. 91-94°, and some oily material. Again the recrystallization of this oily material from pentane was unsuccessful.

1-Chloro-2-p-biphenylylethane was finally successfully prepared by following a modified procedure of M. A. McMahon and S. C. Bunce.[32] In a typical preparation, 2-p-biphenylylethanol (36.3 g, 0.183 mole) was dissolved in 97.2 g (1.23 moles) of pyridine in a 500 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, condenser, dropping funnel, and thermometer. The solution under stirring was cooled in an ice-bath and then thionyl chloride (83.0 g, 0.698 mole) was added slowly at such a rate that the temperature did not rise over 5° throughout the addition. The addition was completed in 170 minutes. The solidified product was heated on a steam bath for 10 minutes and the brown solution was cooled to room temperature. After standing at room temperature for 30 minutes, the deep brown solution was poured into 400 ml of ice water and extracted with four 150 ml portions of ether. The ethereal extracts

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*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

(32) M. A. McMahon and S. C. Bunce, J. Org. Chem., 29(6), 1515 (1964).

were combined, washed with 5 percent $NaHCO_3$, water, dried over anhydrous $MgSO_4$, and filtered. The removal of solvent under partial vacuum yielded 30.4 g (0.140 mole, 76.6 percent yield) of brownish oily product. One recrystallization from pentane gave 25.2 g of light yellow crystals, m.p. 29-31°, and 4.09 g, m.p. 26-30.5°. Vacuum sublimation of these two solid fractions at 95° at 80 microns gave 27.5 g of white solid material, m.p. 30-31.5°, which after one more recrystallization from pentane gave 25.6 g, m.p. 30.7-31.5°. The nmr spectrum [a multiplet centered at 2.88 τ (9.39 H), aromatic hydrogens; a triplet centered at 6.44 τ (2.00 H, J = 7.5 cps), methylene group adjacent to chlorine; another triplet centered at 7.06 τ (2.00 H, J = 7.5 cps), methylene group adjacent to aromatic ring] indicated that this sample was essentially pure 1-chloro-2-p-biphenylylethane. A sample of 0.412 g was further sublimed at 90° and 35 microns to give 0.405 g (taking mechanical loss into account, it was essentially completely sublimed), m.p. 30.8-31.3°. This sample was subjected to C, H analysis.

Anal.* Found: C, 77.73, 77.88; H, 6.18, 6.04. Calcd. for $C_{14}H_{13}Cl$: C, 77.58; H, 6.04.

In another run, 2-p-biphenylylethanol (46.4 g, 0.234 mole) in 114 g of pyridine was reacted with 67.3 ml (0.341 mole) of thionyl chloride at 10 to 15° for two hours and the mixture was heated on a steam bath to 85° and refluxed for a total of three hours. After cooling to room temperature, the product was worked up in the same way as in previous run yielding 19.5 g (0.0899 mole, 38.4 percent yield) of oily material. The low yield of the desired product was apparently due to overheating (three

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*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

hours) at reflux. Two vacuum sublimations at 50 to 100 microns and 75 to 115° gave 16.8 g of white solid material, m.p. 29-30°.

Synthesis of 1-Chloro-2-p-Biphenylylethane-1,1-d_2

Methyl p-Biphenylylacetate

This ester was synthesized according to the general procedure given in Organic Syntheses.[33] A solution of 50.5 g (0.238 mole) of p-biphenylylacetic acid and 15 ml conc. sulfuric acid (Fisher, 95-98 percent) in methanol (distilled after magnesium treatment) was refluxed for 45 hours. Methanol was removed on a steam bath and water was added to the residue. Ether extraction gave 55.6 g of light brown liquid. Vacuum distillation at 150° and 110 microns gave 49.4 g (0.218 mole, 91.5 percent yield) of white solid material, m.p. 26-7°.

2-p-Biphenylylethanol-1,1-d_2

Title compound was successfully prepared by the reduction of methyl p-biphenylylacetate with lithium aluminum deuteride in tetrahydrofuran. Into a flame-dried 2-l Morton flask equipped with a high-speed stirrer, condenser, and dropping funnel was distilled from over $LiAlH_4$ 1200 ml of tetrahydrofuran. Lithium aluminum deuteride (9.56 g, 0.228 mole, Stohler Isotope Chemicals, 99 percent D) was introduced and the solution was stirred at reflux for two and one-half hours before an aliquot of 5 ml was withdrawn for titration. This titration indicated that it was > 98 percent pure $LiAlD_4$. The solution was stirred at reflux for another hour and then a solution of 43.4 g (0.192 mole) of methyl p-biphenylylacetate in 200 ml

(33) E. C. Horning, Organic Syntheses, Collective Volume III, John Wiley & Sons, Inc., New York, 1962, p. 605.

of tetrahydrofuran was added at boiling point of THF dropwise over a period of 40 minutes. The resulting solution was stirred at reflux for another five hours and then allowed to stand at room temperature overnight. Water (50 ml) was added to the solution cautiously to decompose unreacted $LiAlD_4$. The mixture was then poured into a 1:1 mixture of a 10 percent HCl and ice. Ether extraction produced 39.3 g (0.196 mole) of predominantly white crystalline material, m.p. 93.5-96° (premelted at 91°). One recrystallization from carbon tetrachloride gave 36.7 g, m.p. 95.5-96.3°. The nmr spectrum [a multiplet centered at 2.62 τ (9.3 H), aromatic hydrogens; a singlet at 7.19 τ (2.0 H), methylene group adjacent to aromatic ring; another singlet at 7.75 τ (1.0 H), OH group] indicated that it is essentially pure 2-p-biphenylylethanol-1,1-d_2.

1-Chloro-2-p-Biphenylylethane-1,1-d_2

1-Chloro-2-p-biphenylylethane-1,1-d_2 was synthesized by following the same method used for the synthesis of the corresponding protium compound described previously. A solution of 35.20 g (0.1757 mole) of 2-p-biphenylylethanol-1,1-d_2 in 270 ml of pyridine was cooled to 2° under a mild stirring and thionyl chloride (45 ml) was added slowly at such a rate that the temperature was maintained below 8° over a period of 85 minutes. The mixture was warmed on a steam bath to 95° and stirred at 95 ± 3° for five minutes and then cooled to room temperature. After standing at room temperature for 30 minutes, the solution was poured into 1-l ice water and extracted with four 150 ml portions of ether. The ethereal extracts were combined, washed twice with 100 ml portions of water, three 100 ml portions of 10 percent HCl, 100 ml of saturated NaCl, 100 ml of 6 percent $NaHCO_3$,

and water again. After drying over anhydrous $MgSO_4$, the solution was filtered and solvent removed under partial vacuum to give 29.39 g (0.1343 mole, 76.45 percent yield) of pale amber colored solid, m.p. 29-30.5°, with residue. One vacuum sublimation of a 29.10 g sample at 85 to 95° and 80 microns pressure gave 25.90 g of white crystalline material, m.p. 31-2°. The nmr spectrum [a multiplet centered at 2.72 τ (9.00 H), aromatic protons; a singlet at 7.02 τ (2.00 H), methylene group adjacent to aromatic ring] indicated that it is pure 1-chloro-2-p-biphenylylethane-1,1-d_2.

Synthesis of 2,2-Dimethyl-3-phenylpropanoic Acid[34]

2-Benzyl-2-Propanol

This compound was prepared in 71 percent yield by a Grignard reaction between benzyl chloride and acetone.

2-Benzyl-2-Chloropropane

2-Benzyl-2-propanol was converted into 2-benzyl-2-chloropropane in 60 percent yield by following the procedure of L. P. Williams, Jr. The chloride boiled at 72.5 to 74° at 5 mm (Williams reports a b.p. of 65-6° at 4 mm).

2,2-Dimethyl-3-Phenylpropanoic Acid

The title compound was prepared in 5.6 percent yield from 2-benzyl-2-chloropropane by the procedure of L. P. Williams, Jr. After purification by vacuum sublimation at 65° at 30 microns pressure, this acid had a melting point of 57-58.5° (Williams reports an m.p. 56.5-58.0°).

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(34) L. P. Williams, Jr., Ph.D. Thesis, Georgia Institute of Technology, p. 51 (1962).

Synthesis of Alkyl Anions

Reaction of 1-Chlorobutane with Cesium Alloys

The reactions of both cesium-potassium and cesium-potassium-sodium alloys were carried out in ethereal solvents. When tetrahydrofuran or diethyl ether was used as solvent, the solvent was distilled from over $NaAlH_4$ into the reaction vessel first and then the alloy was prepared by adding the metals in the solvent followed by sitrring at the boiling point of the solvent for approximately one hour to give a finely divided metal particle. Then the solution was cooled to the reaction temperature under vigorous stirring. In the case of dimethyl ether as solvent, the alloy was prepared by mixing the metal in the reaction vessel before the solvent was introduced directly from a cylinder and was condensed onto the alloy.* In both tetrahydrofuran and dimethyl ether, the alloy gave a blue color at the beginning of reflux and the color turned greenish after prolonged stirring at reflux and an intense blue color reappeared at low temperatures. But the alloy did not show any detectable color in diethyl ether. The reaction of the chloride with the alloy was followed by carbonation and the carbonated product was worked up by first decomposing the unreacted metals cautiously with water and most of the THF was removed under partial vacuum at water-bath temperature. The residue was washed three times with diethyl ether, acidified, extracted with ether. This ethereal solution was washed with water, reacted with diazomethane and the ester analyzed for methyl valerate by vapor-phase chromatography (VPC). In run 11, toluene (10 ml) was added at ca. -70° before the addition of the chloride.

*The only exception was in run 6, where dimethyl ether was refluxed with $NaAlH_4$ for 30 minutes before distilling into the reaction vessel.

In runs 13 and 14 decalin was added with the reactant as internal standard for the splitting of the two fractions. The quantities of reactants and products together with the conditions of reaction are given in Table 3.

Reaction of Di-n-butylmercury with Cs-K-Na-Alloy

In run 1, cesium alloy prepared in the usual manner from 5.89 g (0.0443 g atom) of cesium, 1.86 g (0.0477 g atom) of potassium and 0.348 g (0.0151 g atom) of sodium in 250 ml tetrahydrofuran was cooled to -69.5° whereupon a blue color appeared and a mixture of 8.26 g (0.0263 mole) of di-n-butylmercury and 0.449 g of decalin was added in one minute. The color of the solution turned from blue to black during this addition. The solution was stirred at -67.5° for three minutes and ca. one half of the solution was carbonated. The remainder of the solution was stirred at Dry Ice-acetone bath temperature for another nine and one-half minutes before carbonation. The hydrocarbons were separated by extractions with ether and valeric acid was obtained by acidification of the aqueous phases followed by ether extractions. Analysis by VPC showed that the total decalin recovered in the two fractions was 75.5 percent. VPC of the acidic product as methyl ester showed that valeric acid was obtained in 20.3 percent and 34.1 percent absolute yields in the first and the second fractions, respectively.

In run 2, a mixture of 3.45 g (0.0110 mole) of di-n-butylmercury and 0.464 g of decalin was added in 40 seconds to a solution of cesium alloy prepared in the usual manner from 5.33 g (0.0401 g atom) of cesium, 1.76 g (0.0451 g atom) of potassium, and 0.220 g (0.0096 g atom) of sodium in 250 ml of tetrahydrofuran at -72°. The same color change as in run 1

Table 3. Reaction of 1-Chlorobutane with Cesium Alloys

Materials and Conditions		Run Number					
		I	II	III	IV	V	VI
1-Chlorobutane	g (mole)	1.69 (0.0182)	1.36 (0.0147)	1.39 (0.0150)	3.68 (0.0397)	3.31 (0.0358)	3.67 (0.0397)
Cesium	g (g atom)	5.43 (0.0321)	4.27 (0.0340)	4.53 (0.0416)	5.54 (0.0416)	4.88 (0.0368)	5.62 (0.0423)
Potassium	g (g atom)	1.43 (0.0408)	1.16 (0.0321)	1.23 (0.0341)	1.79 (0.0458)	1.65 (0.0423)	1.62 (0.0415)
Sodium	g (g atom)				0.235 (0.0102)	0.218 (0.00948)	0.229 (0.00996)
$\frac{M}{RX}$	g atom per mole	4.25	4.21	4.37	2.46	2.47	2.36
Solvent		THF	THF	Et_2O	Et_2O	Me_2O	Me_2O
Temperature		-43°	-38 ± 2°	-36°	-73 ± 2°	ca. -75°	ca. -60°
Time of Addition	min	8	20	2.5	10	0.5	5
Time of Stirring	min	2	2	1	10	9.5	10
Absolute Yield of Valeric Acid	%	1.77	0.64	5.57	19.0	5.68	3.91

Table 3. (Continued)

Materials and Conditions		Run Number					
		VII	VIII	IX	X	XI	XII
1-Chlorobutane	g (mole)	3.14 (0.0339)	3.96 (0.0427)	3.54 (0.0382)	3.57 (0.0385)	3.47 (0.0375)	2.97 (0.0321)
Cesium	g (g atom)	4.53 (0.0341)	5.74 (0.0431)	5.17 (0.0389)	5.25 (0.0395)	5.14 (0.0386)	4.33 (0.0325)
Potassium	g (g atom)	1.48 (0.0379)	1.89 (0.0484)	1.69 (0.0433)	1.78 (0.0456)	1.71 (0.0438)	1.47 (0.0377)
Sodium	g (g atom)	0.197 (0.00856)	0.230 (0.0100)	0.218 (0.009)	0.216 (0.009)	0.208 (0.009)	0.183 (0.00796)
$\frac{M}{RX}$	g atom per mole	2.38	2.37	2.39	2.44	2.44	2.43
Solvent		Me_2O	THF	Me_2O	Et_2O	Me_2O	Me_2O
Temperature		-65 ± 5°	-72°	-107 ± 8°	-95 ± 2°	-66 ± 2°	-98 ± 2°
Time of Addition	min	2	1	0.5	2	3	0.5
Time of Stirring	min	3	1	40	10	13**	5***
Absolute Yield of Valeric Acid	%	13.3	0.433	7.71	2.21*	2.15	4.12
Phenylacetic Acid	%					11.06	
Absolute Yield of n-Octane	%	1.33		None	Trace		
Unreacted n-BuCl	%			None	36.0		

*Ca. 50% of the total acid was lost due to spillage during work up. **The carbonation was delayed for an additional 10 min. ***The carbonation was delayed for an additional 25 min.

Table 3. (Concluded)

Materials and Conditions		Run Number					
		XIII		XIV		XV	
1-Chlorobutane	g (mole)	3.45 (0.0372)		3.20 (0.0345)		2.13 (0.0230)	
Cesium	g (g atom)	5.07 (0.0381)		4.73 (0.0356)		5.19 (0.0390)	
Potassium	g (g atom)	1.68 (0.0431)		1.564 (0.0401)		1.705 (0.0437)	
Sodium	g (g atom)	0.214 (0.00930)		0.193 (0.00839)		0.2115 (0.0092)	
$\frac{M}{RX}$	g atom per mole	2.43		2.44		4.00	
Decalin	g	0.252		0.441			
Solvent		Me_2O		THF		Me_2O	
Temperature		-90 ± 2°		-70°		-60 ± 3°	
Time of Addition	min	0.7		3		5.5	
Time of Stirring	min	10	40	3	12	3	23
Absolute Yield of Valeric Acid	%	1.90	0.878	5.36	2.36	1.76	0.16
Absolute Yield of Octane	%	1.56	1.19	9.10	9.36	3.03	0.75
Unreacted n-BuCl	%	11.14	6.14	0.00	0.00	0.00	0.00
Decalin Recovered	%	28.2		107			

was observed. The solution was stirred at -70 ± 2° for 15 minutes and ca. one half of it was carbonated. The remainder of the solution was stirred at -68 ± 2° for another hour before carbonation. The carbonated product was worked up in the same manner as in run 1 and gave 12.3 percent and 0.45 percent absolute yields of valeric acid in fraction 1 and 2, respectively. The unreacted di-n-butylmercury was recovered in the corresponding fractions in yields of 27.0 percent and 0.07 percent. The overall recovery of decalin was only 27.6 percent. (Decalin was added to the solution to serve as an internal standard for the splitting of the two fractions. However, it was not completely recovered after reaction. In the calculation of yields an assumption was made that the loss of decalin in each fraction was identical.)

In run 3, the alloy was prepared in the usual manner in 250 ml of diethyl ether from 5.58 g (0.0419 g atom) of cesium, 1.85 g (0.0474 g atom) of potassium, and 0.232 g (0.0100 g atom) of sodium. The temperature was lowered to -73° and di-n-butylmercury (7.90 g, 0.0251 mole) was added in 32 seconds. The usual black color was observed. The solution was stirred at -70° for 15 minutes and ca. one half of it was carbonated (Fraction 1). The remainder of the solution was carbonated (Fraction 2) after another 39 minutes of stirring at -70°. A usual work-up gave absolute yields of 37.0 percent of valeric acid and 44.2 percent of unreacted di-n-butylmercury in the first fraction, and 11.0 percent of valeric acid and 2.20 percent of unreacted di-n-butylmercury in the second fraction.

In run 4, the alloy was prepared in the vessel without solvent in the way mentioned previously from 5.25 g (0.0395 g atom) of cesium, 1.72 g (0.0441 g atom) of potassium, and 0.215 g (0.009 g atom) of sodium. Di-

methyl ether was then condensed onto the alloy and the mixture was stirred at boiling point (-23°) of dimethyl ether for one hour. At the beginning of this stirring a pale blue color developed and metals were finely divided, but big particles appeared near the end of this period apparently due to the evaporation and loss of the solvent. Some more dimethyl ether was condensed to make up the lost solvent and the mixture was stirred at -23° for another 30 minutes to ensure well dispersed metal. The temperature was lowered to -71° and the mixture was stirred at -71° for 49 minutes; then 7.20 g (0.0218 mole) of di-n-butylmercury was added in 45 seconds. A dark black color developed in the solution from the beginning of this addition. The resulting solution was stirred at -72° for 15 minutes and ca. one half of it was carbonated. The remainder of the solution was carbonated after another 30 minutes of stirring at -70°. A usual work-up gave in the first fraction absolute yields of 0.258 percent of valeric acid and 11.65 percent of unreacted di-n-butylmercury, and in the second fraction 0.198 percent of valeric acid and 7.42 percent of unreacted di-n-butylmercury.

In run 5, the alloy was prepared in 250 ml of diethyl ether in the usual manner from 22.1 g (0.1667 g atom) of cesium, 7.28 g (0.186 g atom) of potassium, and 0.908 g (0.0395 g atom) of sodium. The temperature was lowered to -70° and di-n-butylmercury (29.6 g, 0.0944 mole) was added dropwise over a period of three minutes. The temperature increased to -65° throughout this addition. The mixture was stirred at -70 ± 3° for three minutes and then four aliquots of approximately 0.5 ml each were withdrawn in 12 minutes for nmr analysis (two kept at Dry Ice-acetone bath temperature and the other two at liquid nitrogen temperature). The remainder of

the solution was immediately carbonated. A usual work-up gave, by VPC analysis, absolute yields of 23.0 percent of valeric acid and 0.0053 percent of unreacted di-n-butylmercury. The nmr analysis did not show any significant absorption upfield from TMS.

Reaction of 1-Chloroheptane with Cesium Alloy

To a mixture of Cs-K-Na alloy prepared in the usual manner at -65° in tetrahydrofuran (250 ml) from 5.83 g (0.0439 g atom) of cesium, 1.93 g (0.0494 g atom) of potassium, and 0.239 g (0.0104 g atom) of sodium was added dropwise over a period of 15 minutes, under vigorous stirring, a solution of 6.65 g (0.0494 mole) of 1-chloroheptane in 25 ml of tetrahydrofuran. The first portion of halide added caused a color change in the solution from deep blue to reddish brown and then to black; the final color was purple. This solution was stirred at -65° for two minutes and about one half was carbonated. The remaining solution was stirred at -65° for another 16 minutes before carbonation. After decomposing excess metals by cautious addition of water, the neutral products were separated by extractions with ether and the extracts washed with water, dried over anhydrous $MgSO_4$, and filtered. Most of the solvents were removed by distillation through a vacuum jacketed column packed with glass helices and the residues analyzed by VPC. The aqueous phases were acidified, extracted with ether, solvents removed in the same way as the neutral products, and the residues reacted with an ethereal solution of diazomethane; the resulting esters were analyzed by VPC. Analytical results are given in Table 4.

Table 4. Absolute Yields of Acid and Neutral Material from the Reaction of 1-Chloroheptane with Cesium Alloy

Material	Run I		Run II	
	Part I %	Part II %	Part I %	Part II %
Octanoic acid	1.49	0.89	4.61	7.49
Heptane	23.6	26.4	9.17	1.78
1-Heptene	13.6	13.7	2.47	0.49
Tetradecane	11.6	11.7	6.09	4.99
Unreacted chloride	28.6	0.54	1.4	0.6

In the second run, a previously prepared Cs-K-Na alloy* (5.0 ml, ca. 0.099 g atom) was introduced with a pipette into a 500 ml Morton flask equipped with a short high-speed stirrer. Trimethylamine, Matheson 99 percent pure refluxed with benzyl chloride for six hours and then stored in a freezer overnight. The next day trimethylamine was distilled into a 500 ml round-bottomed flask containing excess $NaAlH_4$, and then distilled into the alloy. The mixture was stirred at reflux for 30 minutes and this colorless solution was cooled to -35°; stirring was continued at -35 ± 5° for another 30 minutes. 1-Chloroheptane (3.28 g, 0.0244 mole) was added at -35° in three minutes. The first portion of halide added caused an instantaneous development of a black color. The resulting solution was stirred at -45 ± 5° for 12 minutes and then ca. one half was carbonated. The remaining solution was stirred at -40 ± 5° for an additional 20 minutes before carbonation. The carbonated products were worked up in the same

*Prepared by Dr. James A. Pegolotti with a composition of 71.85 percent Cs, 24.55 percent K, and 3.59 percent Na in Nujol.

manner as in the first run and analyzed by VPC (see Table 4).

Neophyllithium

Preparation and Photochemistry

Neophyllithium was prepared according to the procedure of Williams.[20] In run 1, into 250 ml of freshly distilled tetrahydrofuran was placed 1.27 g (0.183 g atom) of lithium. After cooling to -10°, methyl iodide (0.6 ml) and ca. 20 drops of a solution of 11.5 g (0.0684 mole) of neophyl chloride in 25 ml of dry tetrahydrofuran was added. After stirring at -10 ± 5° for 20 minutes, the solution turned pink in color and this color deepened slightly with continued stirring. The mixture was stirred at -10 ± 5° for a total of one hour and the temperature was lowered to -65°; the remaining halide solution was added dropwise over a period of 30 minutes. The solution turned yellow before the completion of the chloride addition. The resulting mixture was stirred at -65 ± 5° for two and one-half hours. At this point, analysis according to the method of Gilman[35] showed that organolithium compound had been formed in 58 percent yield. The mixture was stirred at -65 ± 5° for another two hours and then siphoned under nitrogen atmosphere into a photochemical cell fitted with a quartz well for the UV lamp. The solution was irradiated with a 200 watt Hanovia lamp at ca. -70° for two hours and then was siphoned into a flask containing a large excess of cracked Dry Ice. The next day, water (50 ml) was added to decompose the remainder of the lithium, and the solvents were removed in vacuo at 35° water-bath temperature. Ether extraction of the residue gave 0.558 g (0.00417 mole, 6.09 percent) of neutral material.* Acidification

(35) H. Gilman and H. A. Haubein, J. Am. Chem. Soc., 66, 1515 (1944).

*Most of the neutral material lost due to inadequate work-up procedure.

and ether extraction gave 5.62 g (0.0316 mole, 46.2 percent yield) of acidic material, m.p. 42-47.5°. A 4.38 g sample of this acid was vacuum sublimed at 70° at 150 microns and gave 4.22 g, m.p. 52-60°. A mixture melting point of this acid and authentic 3-methyl-3-phenylbutanoic acid (m.p. 58-59.5°) was 56-59°. VPC analysis of this acidic product as methyl esters showed relative yields of 97.8 percent 3-methyl-3-phenylbutanoic acid and 2.2 percent 2,2-dimethyl-3-phenylpropanoic acid. The neutral material was also subjected to VPC analysis and was found to contain eight compounds; only 0.26 percent absolute yield of the mixture was identified as t-butylbenzene. The remaining components all had longer retention times than neophyl chloride and any of the butylbenzenes.

In run 2, neophyllithium, prepared in ca. 74 percent yield in the same manner and on the same scale as in run 1, was allowed to stand under an atmosphere of dry nitrogen at -70° in the same photochemical cell used above for 13 hours and then was irradiated at -70 ± 5° with a 450 watt Hanovia lamp for 12 hours; the resulting solution was carbonated. The next day, water (100 ml) was added to the mixture and solvents were removed and collected cautiously in vacuo at 35° water-bath temperature; the residue was extracted with three 100 ml portions of ether. The organic solutions (recollected solvents and ether extract) were combined, dried over anhydrous magnesium sulfate and filtered. The solvents were then removed by distilling through a vacuum jacketed column packed with glass helices followed by distilling through a Teflon spinning band column to give a residue of 6.18 g of neutral material which, according to VPC analysis, contained 17 percent of t-butylbenzene. Acidification and ether extraction gave 3.84 g (38.2 percent absolute yield) of acidic material,

m.p. 55-9°. VPC analysis of this acidic material as methyl esters showed relative yields of 98.8 percent 3-methyl-3-phenylbutanoic acid and 1.2 percent 2,2-dimethyl-3-phenylpropanoic acid.

In run 3, the above experiment was repeated and there was obtained 2.34 g of neutral material which, according to VPC contained 35 percent absolute yield of t-butylbenzene, and 5.73 g of acidic material. VPC of the methyl esters showed relative yields of 97.3 percent 3-methyl-3-phenylbutanoic acid and 2.7 percent of 2,2-dimethyl-3-phenylpropanoic acid.

In run 4, neophyllithium was prepared in 80 percent yield in the same manner and on the same scale except that twofold excess of lithium and 300 ml rather than 250 ml of tetrahydrofuran were used. An aliquot of 200 ml of the solution was transferred with a pipette into the regular photochemical cell under nitrogen atmosphere and was allowed to stand at -73 ± 3° for 24 hours with light off before carbonation. The remainder of the solution (ca. 80 ml) was immediately carbonated. A usual work-up gave in the short time portion 0.281 g (0.00209 mole, 13.1 percent) of neutral material which, according to VPC, gave 87.4 percent relative yield of t-butylbenzene, and 2.08 g (0.0117 mole, 73.5 percent) of acidic material, m.p. 48-57.5°. The carbonation product after 24 hours of standing was worked up in the same manner to give 5.19 g (0.0292 mole, 66.7 percent) of acidic material, m.p. 52-57.5°, and 1.17 g (0.00873 mole, 20.0 percent) of neutral material which, according to VPC, gave 81.3 percent relative yield of t-butylbenzene.

In run 5, neophyllithium prepared in 86.1 percent yield from 20.4 g (0.121 mole) of neophyl chloride and 3.96 g (0.571 g atom) of lithium in the usual manner at -60° in 500 ml of tetrahydrofuran was stirred at

-63 ± 2° for another two hours. Then ca. one half of this solution was transferred through a siphon tube packed loosely with glass wool approximately one inch in length into the regular photochemical cell at -65° over a period of 90 minutes and this solution was irradiated with a 450 watt Hanovia lamp at -74 ± 5° for 13½ before carbonation. The remainder of the neophyllithium solution was transferred into another photochemical cell in the same manner under similar conditions and this solution was allowed to stand with light off at the same temperature for the same length of time as the portion for photochemical reaction before carbonation. A usual work-up gave, in the photochemical reaction, 4.89 g (0.0275 mole) of acidic material, m.p. 48-60.5°, and 3.37 g (0.0251 mole) of neutral material and, in the thermodecomposition reaction, 7.79 g (0.0438 mole) of acidic material, m.p. 38-59°, and 6.54 g (0.0488 mole) of neutral material. The acidic products were analyzed by VPC as methyl esters and were found to give, in the photochemical reaction, relative yields of 97 percent 3-phenyl-3-methylbutanoic acid and three percent 2,2-dimethyl-3-phenylpropanoic acid and, in the thermodecomposition reaction, 96.5 percent 3-phenyl-3-methylbutanoic acid and 3.5 percent 2,2-dimethyl-3-phenylpropanoic acid.

Stability and Rearrangement

In run 1, the reaction of 10.3 g (0.0613 mole) of neophyl chloride with 1.80 g (0.259 g atom) of lithium metal in 250 ml of tetrahydrofuran was initiated in the usual manner at -10°. Then the temperature was lowered to -62° and the remainder of the chloride solution was added dropwise over a period of 30 minutes. A yellowish green color developed in the solution near the end of this addition. The stirring was continued

at -60 ± 2° for five minutes and the first aliquot of 25 ml of the solution was carbonated. The temperature was lowered to -70° and the solution was stirred at -70 ± 5° for four hours before a second aliquot of 25 ml was carbonated. After another four hours of stirring at -70 ± 5°, the final (third) fraction of the solution was carbonated. A usual work-up yielded 0.0789 g (0.000443 mole, 72.3 percent), 0.0777 g (0.000436 mole, 71.2 percent), and 0.0750 g* (0.000421 mole, 0.865 percent) of crystalline acidic material in fractions 1, 2, and 3, respectively. VPC of methyl esters showed relative yields of 93.6 percent, 94.5 percent, and 96.1 percent 3-methyl-3-phenyl-butanoic acid in fractions 1, 2, and 3, respectively; the relative yields of 2,2-dimethyl-3-phenylpropanoic acid in the corresponding fractions were 6.40 percent, 5.54 percent, and 3.89 percent, respectively.

In run 2, the reaction of neophyl chloride (10.2 g, 0.0605 mole) and lithium metal (1.82 g, 0.262 g atom) in 250 ml of tetrahydrofuran was initiated in the usual manner at -10°. Then the temperature was lowered to -65° and the remaining chloride solution was added dropwise over a period of 15 minutes. The stirring was continued at -65 ± 3° for two hours and a first aliquot of 25 ml of the solution was carbonated. The remaining solution was warmed to -50° and stirring was continued at -50 ± 3° for 15 minutes before a second aliquot of 25 ml of the solution was carbonated. The temperature of the original reaction vessel was raised to -40° and the solution was stirred at -40 ± 3° for 15 minutes; a third aliquot of 25 ml was carbonated. The remainder of the organolithium solution was

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*Product was lost due to spillage during work-up.

stirred at -40 ± 3° for an additional two hours before carbonation (fraction 4). A usual work-up gave 1.09 g (0.00614 mole, 81.2 percent), 1.08 g (0.00607 mole, 80.2 percent), 1.07 g (0.00599 mole, 79.2 percent), and 5.03 g (0.0282 mole, 74.7 percent) of crystalline acidic material in fractions 1, 2, 3, and 4, respectively. VPC of the methyl esters showed relative yields of 94.0 percent, 94.8 percent, 94.8 percent, and 96.4 percent 3-methyl-3-phenylbutanoic acid in fractions 1, 2, 3, and 4, respectively; the relative yields of 2,2-dimethyl-3-phenylpropanoic acid in the corresponding fractions were 6.04 percent, 5.20 percent, 5.22 percent, and 3.65 percent, respectively.

In run 3, the reaction of 10.0 g (0.0593 mole) of neophyl chloride with 1.14 g (0.164 g atom) of lithium in 250 ml of tetrahydrofuran was initiated in the usual manner at -10° and then the remaining halide solution was added at -10° dropwise over a period of 32 minutes. A light yellow color developed at the beginning of this addition and deepened to orange near the end of addition. The stirring was continued at -15° for two minutes and then a first aliquot of 50 ml of the solution was carbonated. The remainder of the solution was allowed to stand for three minutes and then stirred at -10 ± 2° for 30 minutes before carbonation. The carbonation products were worked up in the usual manner yielding in the first portion 0.714 g (0.00401 mole, 33.1 percent yield) and in the second portion 4.75 g (0.0267 mole, 63.1 percent yield) of crystalline acidic material. VPC of the methyl esters showed relative yields of 1.13 percent 2,2-dimethyl-3-phenylpropanoic acid and 98.3 percent 3-methyl-3-phenylbutanoic acid in fraction 1 and 1.69 percent 2,2-dimethyl-3-phenylpropanoic acid and 97.2 percent 3-methyl-3-phenylbutanoic acid in fraction

2. The neutral material in tetrahydrofuran solution was analyzed by VPC and found to give 0.088 g (0.000656 mole, 5.42 percent) of t-butylbenzene, 0.049 g (0.000363 mole, 3.00 percent) of i-butylbenzene, and 0.991 g (0.00587 mole, 48.5 percent) of unreacted chloride in fraction 1 and 0.874 g (0.00652 mole, 13.8 percent) of t-butylbenzene, 0.372 g (0.00277 mole, 5.87 percent) of i-butylbenzene and 1.068 g (0.00633 mole, 13.4 percent) of unreacted chloride in fraction 2.

In run 4, neophyllithium was prepared at -65° from 10.1 g (0.0597 mole) of neophyl chloride and 1.39 g (0.200 g atom) of lithium in the same way as those described in previous sections. Then a first aliquot of 50 ml of the solution was carbonated and the remainder of the solution was allowed to warm up to ice-bath temperature (4°) and stand without stirring at 4° for four hours before carbonation. A usual work-up gave in the first fraction 1.84 g (0.0103 mole, 74.6 percent yield) and in the second fraction 0.634 g (0.00356 mole, 7.76 percent) of acidic material. These acidic products were analyzed as methyl esters by VPC and were found to give relative yields of 92.5 percent 3-methyl-3-phenylbutanoic acid (relative retention time 1.00), 5.60 percent 2,2-dimethyl-3-phenylpropanoic acid (relative retention time 0.79) and two percent of two unidentified compounds (1.05 percent at 0.87, 0.97 percent at 1.37) in fraction 1; the acids in fraction 2 are given in relative yields (relative retention time): 50.4 percent (0.86), 18.7 percent (1.00), 29.2 percent (1.37). The neutral material was also subjected to VPC analysis and found to give in the first fraction 0.0935 g (0.000698 mole, 5.06 percent yield) of t-butylbenzene, 0.0415 g (0.000309 mole, 2.24 percent yield) of i-butylbenzene, and 0.151 g (6.47 percent) of unreacted chloride, and in the second frac-

tion 4.74 g (0.0354 mole, 77.1 percent) of t-butylbenzene, 0.484 g (0.00361 mole, 7.87 percent) of i-butylbenzene, and 0.227 g (2.92 percent) of unreacted chloride.

Effect of N,N,N',N'-Tetramethylethylenediamine (TMEDA)

To a solution of neophyllithium, prepared at -65° in 500 ml of tetrahydrofuran in the usual manner from 20.8 g (0.123 mole) of neophyl chloride and 1.98 g (0.285 g atom) of lithium, was added N,N,N',N'-tetramethylethylenediamine (14.4 g, 0.124 mole) at -65° in one minute. The mixture was stirred at high speed at -65 ± 5° for another four minutes and then the temperature was raised gradually to -30° over a period of two hours. Stirring was continued at -30 ± 5° for an additional two hours and then the resulting solution was siphoned into a flask containing excess solid carbon dioxide. A usual work-up yielded 16.8 g (0.0944 mole, 76.7 percent yield) of acidic material, m.p. 55-59°, mixture m.p. with authentic 3-methyl-3-phenylbutanoic acid: 51-8°. The mixture of a 1:1 ratio of this acidic product and 2-phenyl-2-methylbutanoic acid melted at room temperature. VPC analysis of the methyl esters showed relative yields of 97.8 percent 3-methyl-3-phenylbutanoic acid and 2.2 percent 2,2-dimethyl-3-phenylpropanoic acid. The neutral product was not analyzed.

In the second run, excess (150 ml, 1.00 mole) TMEDA was added over a two minute period to a solution of neophyllithium prepared in the usual way from 10.0 g of neophyl chloride and 1.11 g of lithium in 250 ml of tetrahydrofuran at -65°. Then this yellow solution was warmed to -20° under vigorous stirring over a period of 20 minutes and stirring was continued at -20° for one hour before an aliquot of 50 ml was carbonated. The remainder of the solution was carbonated after another two hours of

stirring at -20°. A usual work-up gave 1.17 g (0.00658 mole, 82.0 percent) and 4.42 g (0.0248 mole, 51.6 percent) of acidic products in fractions 1 and 2, respectively. VPC of both acidic products (as methyl esters) and neutral products showed that there were produced in the first fraction 1.01 g (0.00569 mole, 70.8 percent) of 3-methyl-3-phenylbutanoic acid, 0.0151 g (0.000084 mole, 1.0 percent) of 2,2-dimethyl-3-phenylpropanoic acid, 0.0772 g (0.000576 mole, 7.18 percent) of t-butylbenzene, 0.0285 g (0.000212 mole, 2.64 percent) of i-butylbenzene, 0.00650 g (0.48 percent) of unreacted chloride, and a total of 6.5 percent of three unidentified compounds and in the second fraction 2.93 g (0.0165 mole, 34.3 percent) of 3-methyl-3-phenylbutanoic acid, 1.70 g (0.0127 mole, 26.4 percent) of t-butylbenzene, 0.361 g (0.00270 mole, 5.48 percent) of i-butylbenzene, together with some 1.9 percent of three unidentified compounds. Neither 2,2-dimethyl-3-phenylpropanoic acid nor unreacted chloride was found in the second fraction.

Effect of Absence of Methyl Iodide

The reaction of a normal scale (10.0 g) of neophyl chloride with lithium (0.964 g, 0.139 g atom) in 250 ml of tetrahydrofuran was initiated at -10° (by reacting a small portion (ca. 4 percent) of the halide with Li) in two hours in the absence of methyl iodide. Then the temperature was lowered to -65° and the remaining halide solution was added dropwise over a period of 30 minutes, and stirring was continued at -67 ± 3° for another four hours before carbonation. The carbonated product yielded some 6.89 g (0.0387 mole, 65.4 percent yield) of solid acidic material which, according to VPC of methyl esters, gave relative yields of 91.6 percent 3-methyl-3-phenylbutanoic acid, 6.0 percent 2,2-dimethyl-3-phenylpropanoic acid,

together with some 2.4 percent of two unidentified acids. The neutral product was analyzed by quantitative VPC and found to yield 0.601 g (0.00448 mole, 7.57 percent) of t-butylbenzene, 0.159 g (0.00119 mole, 2.00 percent) of i-butylbenzene, 1.41 g (14.1 percent) of unreacted chloride, and 0.155 g (1.95 percent) of an unidentified compound.

Effect of Presence of One Percent of Sodium in Lithium Metal

Into 250 ml of freshly distilled tetrahydrofuran was placed 0.955 g (0.138 g atom) of lithium metal containing one percent sodium and a small portion (ca. 4 percent) of a solution of 10.1 g (0.0597 mole) of neophyl chloride in 25 ml of dry tetrahydrofuran. The temperature was lowered to -65° and the mixture was stirred at -65° for two hours. While there was no sign of initiation, the temperature was raised to -10° and the mixture was stirred for another two hours. Even though there was no color appearance to indicate the initiation, the temperature was lowered to -65° and the remaining halide solution was added dropwise over a period of 40 minutes. Stirring was continued at -65 ± 5° for another four hours and then the solution was carbonated. The carbonated product yielded 6.36 g (0.0357 mole, 59.8 percent yield) of crystalline acidic material, m.p. 52-57.5°, and some neutral material which, according to quantitative VPC, produced 0.503 g (0.00375 mole, 6.29 percent) of t-butylbenzene, 0.169 g (0.00126 mole, 2.11 percent) of i-butylbenzene, 0.412 g (4.08 percent) of unreacted chloride, and some one percent of an unidentified compound. The acidic product (as methyl esters) was analyzed by VPC and found to give relative yields of 95.2 percent 3-methyl-3-phenylbutanoic acid and 4.84 percent 2,2-dimethyl-3-phenylpropanoic acid.

Effects of Iodine and Halides

To a solution of neophyllithium prepared in ca. 75 percent yield* in the usual manner at -65° from 10.0 g (0.0595 mole) of neophyl chloride and 0.920 g (0.133 g atom) of lithium in tetrahydrofuran was added a solution of 3.82 g (0.0152 mole) of iodine in 20 ml of dry tetrahydrofuran dropwise at -65° over a period of 11 minutes. Both the brown color of I_2-THF and yellow color of neophyllithium disappeared as soon as the two were mixed together. The temperature dropped 4° throughout this addition. The solution was stirred at -65° for another 15 minutes and then an aliquot of 25 ml of the light colored solution was carbonated. The remaining solution was stirred at -65 ± 5° for an additional 49 minutes before carbonation. The carbonated products were worked up in the usual manner and the results are given in Table 5.

Neophyllithium, prepared in the usual manner at -65° from 20.1 g (0.119 mole) of neophyl chloride and 1.86 g (0.268 g atom) of lithium in tetrahydrofuran was warmed to -10° and stirred at -10 ± 5° for one hour. The reaction temperature was again lowered to -65° and about 10 percent of the solution was carbonated (fraction 1). The remainder of the solution was then divided into two parts of approximately equal volumes and to one of these was added 4.43 g (0.0284 mole) of ethyl iodide which caused a rise of temperature from ca. -60° to -45° during addition, and into another half was added 4.79 g (0.0283 mole) of neophyl chloride at ca. -65°. One half of the solution in which ethyl iodide had been added was carbonated (fraction II) immediately after the solution had been well

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*According to Gilman titration.[35]

Table 5. Neophyllithium, Effects of Iodine

Neophyl Chloride		10.0 g (0.059 mole)			
Lithium Metal		0.920 g (0.1326 g atom)			
Methyl Iodide		0.6 ml			
Stirring at -10°	min	60			
Reaction Temperature		-65°			
Time of Addition	min	33			
Time of Stirring at -65°		5 hours			
I_2 at -65°		0		0.0152 mole	
Reaction Time after I_2 Addition				15 min	64 min
Yield of Crude Acids	%	76.0[b]		16.07**[b]	10.42[b]
$PhCMe_2CH_2CO_2H$	%	32.2[a]	ca.	2.6[a]	3.65[a]
$PhCH_2CMe_2CO_2H$	%	1.52[a]	ca.	0.02[a]	0.081[a]
t-Butylbenzene	%	7.88[a]		11.13[a]	9.83[a]
i-Butylbenzene	%	3.02[a]		2.78[a]	2.31[a]
Neophyl Chloride	%	11.4[a]		8.58[a]	4.45[a]
High M.W. Hydrocarbons*	g				
2.06 †		---		0.217	0.122
6.71 †		0.00563		0.499	2.619
8.47 †		---		0.0312	0.196
11.76 †		---		0.0041	0.037

*By weight

**Some material was lost due to spillage during work-up.

†Relative retention time based on neophyl chloride = 1.00.

[a]Quantitative VPC using external standards based on calibration curve, absolute yield.

[b]By isolation, absolute yields

mixed and the remainder was allowed to stand at the Dry Ice-acetone bath temperature for 15 minutes before carbonation (fraction IV). The portion in which neophyl chloride had been added was allowed to stand at Dry Ice-acetone bath temperature for 15 minutes and then one half of it was carbonated (fraction III); the remainder of the solution was allowed to stand at the same temperature for an additional 45 minutes before carbonation (fraction V). The carbonated products were worked up in the usual manner and analyzed for both hydrocarbons and organic acids, as methyl esters, by VPC. Results are given in Table 6. The neutral products from fractions III and V were combined, solvent distilled through a vacuum jacketed column packed with glass helices, and the residue distilled at 26°/6 mm and 96-105°/3 mm to give 2.66 g of a liquid. VPC showed that this liquid contained as major components t-butylbenzene, i-butylbenzene, and unreacted chloride in the ratio of 3.46 : 2.31 : 1.00. The presence of these three compounds was also confirmed by nmr.

Neophyl chloride (10.0 g, 0.0591 mole) was reacted with lithium (0.908 g, 0.1308 g atom) in the usual manner in tetrahydrofuran at -65° and an aliquot of 50 ml was carbonated. To the remaining solution at -69° was added 9.83 g (0.0582 mole) of neophyl chloride in 25 ml of tetrahydrofuran dropwise over a period of 30 minutes. There was observed an increase in temperature of 2-3° throughout this addition. The resulting solution was stirred at -69° for 30 minutes and then a second aliquot of 50 ml was carbonated. The remaining solution was stirred at the same temperature for a total of four hours (after the completion of the last neophyl chloride addition) before carbonation. The carbonated products were worked up in the usual manner and analyzed by VPC. Results are given in Table 7.

Table 6. Neophyllithium, Effects of Ethyl Iodide and Neophyl Chloride

Fraction		I	II	III	IV	V
Neophyl Chloride Started with	g (mole)	2.35 (0.0132)	4.60 (0.0259)	4.78 (0.0269)	4.52 (0.0254)	3.76 (0.0212)
Lithium Metal	g (g atom)			1.86 (0.268)		
Stirring at -65°		3 hours				
At -10°		1 hour				
EtI added at -60°	mole	none	0.0152	none	0.0129	none
Standing after EtI addition	min		ca. 1		15	
Neophyl Chloride added at -65°	g (mole)		none	2.68 (0.0159)	none	2.11 (0.0124)
Standing after Neophyl Chloride addition	min			15		60
$PhCMe_2CH_2CO_2H$	%	39.36[a]	4.39[a]	31.06[a]	3.11[a]	40.1[a]
$PhCH_2CMe_2CO_2H$ (?)	%	1.35[a]	0.00[a]	1.12[a]	0.00[a]	1.54[a]
t-Butylbenzene 1.00*	%	19.28[a]	19.47[a]	18.03[a]	19.95[a]	19.69[a]
i-Butylbenzene 1.09*	%	8.96[a]	8.57[a]	8.79[a]	8.74[a]	8.76[a]
Neophyl Chloride 4.19*	%	2.86[a]	2.97[a]	77.69[a]	2.58[a]	83.33[a]
2.50*, Neutral	%	0.00[a]	2.62[a]	0.00[a]	2.67[a]	0.00[a]
2.69*, Neutral	%	0.00[a]	21.93[a]	0.00[a]	22.68[a]	0.00[a]

*Relative retention time based on t-butylbenzene as standard. [a]See footnote in Table 5.

Table 7. Neophyllithium, Effects of Neophyl Chloride

Neophyl Chloride Started with		10.0 g (0.0591 mole)		
Lithium Metal		0.908 g (0.131 g atom)		
Solvent		THF		
Methyl Iodide		0.5 ml		
Initiation		-10°, 1 hour		
Reaction Temperature		-65°		
Time of Addition		30 min		
Stirring at -65°		4 hours		
Neophyl Chloride added at -69° (over a period of 30 minutes)		0	9.83 g (0.0582 mole)	
Stirring after addition		---	30 min.	4 hours
Yield of Crude Acids	%	78.15[b,c] (50.63)[b,d]	57.29[b,c] (51.78)[b,d]	62.58[b,c] (56.58)[b,d]
$PhCMe_2CH_2CO_2H$	%	70.7[a,c] (63.92)[a,d]	48.4[a,c] (43.712)[a,d]	56.23[a,c] (50.83)[a,d]
$PhCH_2CMe_2CO_2H$	%	3.33[a,c] (3.00)[a,d]	1.76[a,c] (1.59)[a,d]	1.39[a,c] (1.25)[a,d]
t-Butylbenzene	%	6.41[a,c] (5.80)[a,d]	9.61[a,c] (1.69)[a,d]	14.68[a,c] (13.27)[a,d]
i-Butylbenzene	%	2.94[a,c] (2.66)[a,d]	3.79[a,c] (3.43)[a,d]	4.90[a,c] (4.43)[a,d]
Neophyl Chloride	%	12.80[a,c] (11.65)[a,d]	57.79[a,e] (116.5)[a,d]	41.93[a,e] (84.52)[a,d]

[a,b] See footnote in Table 5.

[c] Based on neophyl chloride started with

[d] Based on Li metal used

[e] Based on total neophyl chloride used

In the regular neophyllithium reaction vessel was placed 300 ml of heptane and 1.71 g (0.247 g atom) of lithium. To the solvent was added 0.5 ml of methyl iodide and 23 drops of a solution of 18.0 g (0.0593 mole) of neophyl chloride in 25 ml of heptane. The mixture was stirred vigorously at 35 ± 10° for one hour, and to the pale yellow solution was added the balance of the halide dropwise over a period of 30 minutes. After the mixture was stirred for three and one-half hours at 33 ± 3°, the solution was found to contain 0.0220 mole (37 percent yield) of neophyllithium. The mixture was allowed to warm to 60° and was stirred at 60 ± 5° and then an aliquot (fraction 1) of 50 ml was carbonated. The remaining solution was cooled to 36° and a saturated solution of iodine (0.490 g, 0.00194 mole) in heptane was added over 30 minutes. The mixture was stirred at 35° for 15 minutes and an aliquot (fraction 2) of 50 ml was carbonated. The remainder of the solution was stirred at the same temperature for an additional 45 minutes before carbonation (fraction 3). A usual work-up yielded 0.0872 g (0.000490 mole, 4.95 percent), 0.118 g (0.000666 mole, 6.74 percent), and 0.0847 g (0.000476 mole, 1.20 percent) of acidic products in fractions 1, 2, and 3, respectively. The neutral products were analyzed by VPC and found to produce t-butylbenzene in 0.0262 g (0.000195 mole, 1.98 percent), 0.0254 g (0.000190 mole, 1.92 percent), and 0.125 g (0.000933 mole, 2.36 percent), and i-butylbenzene in 0.0138 g (0.000103 mole, 1.04 percent), 0.0138 g (0.000103 mole, 1.04 percent), and 0.0801 g (0.000598 mole, 1.59 percent) and unreacted neophyl chloride in 0.325 g (0.00192 mole, 19.4 percent), 0.315 g (0.00186 mole, 18.9 percent), and 1.484 g (0.00878 mole, 22.2 percent) in the corresponding three fractions. The above acidic products were reacted with diazomethane and subjected to VPC analysis.

This analysis showed that the acidic products were not volatile at 193° column temperature (nothing showed up in 14 minutes).

Cleavage with Cs-K-Na Alloy

In run 1, neophyllithium was prepared from 5.59 g (0.0331 mole) of neophyl chloride and 0.478 g (0.0689 g atom) of lithium in the usual manner in 250 ml of tetrahydrofuran at -65°. Then to the flask was added rapidly 5.00 ml (0.099 g atom) of Cs-K-Na alloy.* This addition caused an instantaneous color change from brown to green in the solution. Stirring was continued at -65° for three minutes and then an aliquot of 25 ml of the solution was carbonated. The remaining solution was stirred at -65° for another hour before carbonation. The products were worked up in the usual manner to give, in the first fraction, 0.448 g (0.00252 mole, 83.7 percent yield) and, in the second fraction, 4.13 g (0.0232 mole, 77.1 percent yield) of oily acidic material. An aliquot of each of the acidic products was converted into methyl esters and then subjected to VPC analysis. This analysis showed relative yields of 81.3 percent 3-methyl-3-phenylbutanoic acid (relative retention time ≡ 1.00), 5.00 percent 2,2-dimethyl-3-phenylpropanoic acid (relative retention time 0.89), and a total of some 14 percent of four unidentified acids [proportions (relative retention times): 2.89 percent (0.63), 0.65 percent (0.74), 0.65 percent (0.79), and 9.48 percent (1.17)] in fraction 1. The acidic product from fraction 2 was found to give, by the same method, 80.0 percent 3-methyl-3-phenylbutanoic acid (relative retention time ≡ 1.00), 5.47 percent 2,2-dimethyl-3-phenylpropanoic acid, and a total of some 14.1 percent of

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*See footnote on page 34.

the same four unidentified acids [proportions (relative retention times): 3.35 percent (0.63), 0.70 percent (0.74), 1.35 percent (0.79), 8.74 percent (1.17)] as in fraction 1. The neutral material was found, according to quantitative VPC, to produce in the first fraction 0.0470 g (0.000351 mole, 11.7 percent) of t-butylbenzene and 0.00875 g (0.0000653 mole, 2.17 percent) of i-butylbenzene and, in the second fraction, 0.441 g (0.00329 mole, 10.9 percent) of t-butylbenzene and 0.0740 g (0.000552 mole, 1.83 percent) of i-butylbenzene. According to VPC, there was no unreacted chloride in either fraction.

In run 2, neophyllithium was prepared on the same scale (from 5.72 g of neophyl chloride) and in the same manner as in run 1 at -65° in tetrahydrofuran. To this solution was then added Cs-K-Na alloy (5 ml, ca. 0.099 g atom). A greenish color started to develop when the temperature was about -40° and the solution was black in color at -30°; the color was greenish at -10°. This greenish solution with black powders was stirred at -10° for another 45 minutes and then carbonated. A usual work-up gave 3.64 g (0.0204 mole, 60.5 percent yield) of oily acidic material which, according to quantitative VPC of the methyl esters, contained 2.14 g (0.120 mole, 35.5 percent yield) of 3-methyl-3-phenylbutanoic acid, 0.0489 g (0.000275 mole, 0.81 percent) of 2,2-dimethyl-3-phenylpropanoic acid, together with three unidentified acids in small amounts [0.81 percent (relative retention time 0.77), 0.61 percent (relative retention time 1.16), and 0.61 percent (relative retention time 1.26)]. The neutral product was also subjected to quantitative VPC analysis and found to contain 0.961 g (0.00718 mole, 21.2 percent yield) of t-butylbenzene, and 0.217 g (0.00162 mole, 4.78 percent yield) of i-butylbenzene. There was no detectable amount of unreacted chloride.

Reaction of Neophyl Chloride with Cesium Alloys

In run 1, into 250 ml of freshly distilled tetrahydrofuran was placed 5.58 g (0.0419 g atom) of cesium and 1.53 g (0.0391 g atom) of potassium and the mixture was stirred at reflux for one hour. The resulting blue solution was cooled to -60° and 2.83 g (0.0167 mole) of the chloride in 25 ml of dry tetrahydrofuran was added dropwise over a period of eight minutes and the solution was stirred at -60° for another 30 minutes before carbonation. The addition of the halide caused the development of a yellowish brown color. A usual work-up yielded 1.58 g (57.7 percent) of neutral material which, according to VPC, was mainly t-butylbenzene, and 1.16 g (42.3 percent) of oily acidic material. This acidic material was washed with pentane to give 0.699 g of pentane soluble material and 0.382 g pentane insoluble residue, m.p. 200-250°. A 0.233 g sample of the pentane soluble fraction was sublimed at 70° at 50 microns pressure to give 0.137 g (58.6 percent) of sublimate. A 0.133 g sample of this sublimate was reacted with diazomethane and the methyl esters formed were subjected to VPC analysis (see Table 8).

In run 2, cesium-potassium alloy prepared from 4.80 g (0.0361 g atom) of cesium and 1.30 g (0.0332 g atom) of potassium in 250 ml of tetrahydrofuran was stirred at reflux for 40 minutes and then the temperature was lowered to -40°. A solution of 2.72 g (0.0161 mole) of neophyl chloride in 25 ml of tetrahydrofuran was added dropwise over a period of five minutes at -40 ± 2° and the resulting solution was stirred at the same temperature for two minutes before carbonation. The carbonated product was worked up in the usual manner to give 0.970 g (44.3 percent yield) of neutral material which, according to VPC, gave relative yields of 85 percent

Table 8. Vapor-Phase Chromatographic Analyses of the Acidic Products from Cesium Alloy Reactions of Neophyl Chloride

Relative Retention Time*	Relative Yields (Absolute Yields)					
	Run 1	Run 2	Run 3	Run 4	Run 5	
					Fract. 1	Fract. 2
0.77	21.54 (5.88)	23.19 (4.31)	30.21 (8.03)	10.45 (0.209)	35.12	47.40
0.84	25.60 (6.99)	12.86 (2.39)	20.36 (5.41)	11.36		
0.91	10.39 (2.84)	7.43 (1.38)	4.10 (1.09)	0.91 (0.018)	9.76	8.98
0.97 1.00	1.81 (0.49)	0.54 (0.10)	4.60 (1.22)	43.18** (0.864)	2.19	1.32
1.23	37.65 (10.29)	21.56 (4.00)	30.71 (8.16)	25.91 (0.518)	25.37	18.85
1.50	1.36 (0.37)	0.91 (0.17)	4.93 (1.31)	6.59 (0.138)	2.44	2.66
1.60	0.60 (0.16)	32.97 (6.12)	3.78 (1.00)		7.80	11.49

VPC conditions used: temperature 194°; flow rate 15.0 mm; pressure 60 psig; column 12'$\frac{1}{4}$", Apiezon L. (10%).

*Based on the retention time of methyl 3-methyl-3-phenylbutanoate ≡ 1.00.

Relative retention time of methyl 2-methyl-2-phenylbutanoate was 0.91. Relative retention time of methyl o-t-butylbenzoate was 0.97.

**Only a single compound identified as methyl 3-methyl-3-phenylbutanoate.

t-butylbenzene and 9.5 percent s-butylbenzene and/or i-butylbenzene and 1.22 g (42.6 percent yield) of acidic product. A 0.721 g sample of this acidic material was sublimed at 75-85° at 20 microns pressure to give 0.314 g of sublimate. A 0.143 g of this sublimate was converted into methyl esters and analyzed by VPC (see Table 8).

In run 3, into a regular 500-ml Morton flask containing 250 ml of freshly distilled tetrahydrofuran was pipetted 4.5 ml (ca. 0.087 g atom) of a previously prepared Cs-K-Na alloy.* The mixture was stirred at reflux for one hour and then cooled to -66°, and a solution of 4.06 g (0.0240 mole) of neophyl chloride in 25 ml of dry tetrahydrofuran was added dropwise over a period of five minutes. The first portion of halide added caused the development of a green color in the solution and the solution was brown in color at the end of the addition. The stirring was continued at -67° for another eight minutes before carbonation. The carbonation product showed a purple color. A usual work-up yielded 1.81 g (0.0102 mole, 42.4 percent) of acidic material of which 52.8 percent was sublimable at 10 microns at 90-140° and some neutral material which, according to VPC, contained 1.22 g (0.00910 mole, 37.9 percent yield) of t-butylbenzene, 0.0642 g (0.000479 mole, 2.00 percent) of s-butylbenzene and/or i-butylbenzene and 0.09 g (2.22 percent) of unreacted neophyl chloride. The acidic material was analyzed as methyl esters by VPC (see Table 8).

In run 4, the same Cs-K-Na alloy (4.5 ml, ca. 0.087 g atom) as in run 3 was introduced into the same reaction vessel containing 250 ml of dry diethyl ether and the mixture was stirred at reflux for one hour.

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*See the footnote of page 34.

The temperature was then lowered to -71°, where the solution was colorless and metals were finely divided, and ca. 2 percent of a solution of 3.74 g (0.0221 mole) of neophyl chloride in 20 ml of dry ether was added. This addition caused the development of a yellow color in the solution and a rise of temperature to -65°. The temperature was lowered to -70° and the balance of the halide was added dropwise over a period of five minutes and the resulting solution was stirred for one minute before carbonation. A usual work-up gave 0.186 g (0.00104 mole, 4.73 percent yield) of acidic material of which 42.6 percent was sublimable at 95° at 100 microns pressure and some neutral material which, according to VPC, contained 0.56 g (18.9 percent yield) of t-butylbenzene, 0.0314 g (0.000234 mole, 1.06 percent) of s-butylbenzene and/or i-butylbenzene and 1.89 g (50.5 percent recovery) of unreacted chloride. The acidic material was analyzed as methyl esters by VPC (see Table 8).

In run 5, the same quantity of the same Cs-K-Na alloy was placed in 300 ml of freshly distilled tetrahydrofuran and the mixture was stirred at reflux for one hour. The temperature was then lowered to -60° and stirring was continued until the metals were finely divided. A solution of 3.81 g (0.0214 mole) of neophyl chloride in 25 ml of tetrahydrofuran was added at -60° dropwise over a period of five minutes. A reddish brown color developed at the beginning of this addition which gradually changed to greenish throughout the addition. The resulting solution was stirred at -60 ± 2° for two minutes and then about one half was carbonated. The remaining solution was stirred at ca. -60° for 30 minutes before carbonation. A usual work-up gave, in the first fraction, 0.750 g (0.00421 mole, 39.3 percent yield) and, in the second fraction, 1.47 g (0.00829 mole, 77.4

percent yield) of oily acidic products. These acidic products were reacted with diazomethane and the methyl esters analyzed by VPC (see Table 8). VPC of the neutral products showed that t-butylbenzene constituted at least 90 percent of the volatile hydrocarbons.

Reaction of Neophyl Chloride with Sodium in Dioxane-t-Amyl Alcohol

Into a regular vessel for lithium reactions was placed 14.7 g (0.0869 mole) of neophyl chloride, 110 ml of dioxane, 140 ml of t-amyl alcohol, and 8.17 g (0.357 g atom) of sodium. The mixture was heated until reflux was attained and the purple colored solution was stirred at reflux for two hours, and then ethanol (50 ml) was added to decompose unreacted sodium. A small amount of dilute HCl was added and the organic phase was separated. The aqueous phase was extracted with three 100 ml portions of ether and the organic phases were combined, washed with a saturated solution of sodium chloride, dried over anhydrous $MgSO_4$. After filtration, most of the solvents was removed by distillation through a vacuum jacketed column packed with glass helices and the residue was analyzed by VPC. This analysis showed that it contained 8.03 g (0.0599 mole, 68.9 percent yield) of t-butylbenzene contaminated by less than 1.2 percent relative yield of isomeric impurities.

Reaction of Neophyl Chloride with Potassium

In 250 ml of freshly distilled tetrahydrofuran was placed, under nitrogen atmosphere, 5.66 g (0.145 g atom) of potassium and the mixture was stirred at reflux for one hour, and then a solution of 10.1 g (0.0602 mole) of neophyl chloride in 25 ml of tetrahydrofuran was added dropwise

over a period of 22 minutes. The first portion of halide added caused the development of a yellow color in the solution and the final color was reddish brown. The resulting solution was stirred at reflux for another two minutes before carbonation. A usual work-up yielded 0.723 g (0.00406 mole, 6.74 percent) of oily acidic material which, according to VPC of the methyl esters, contained three major acids in yields of 0.00874 g (0.0000491 mole, 0.0816 percent), 0.0155 g (0.0000871 mole, 0.145 percent), and 0.0321 g (0.0001805 mole, 0.300 percent), with relative retention times of 0.76, 0.85, and 1.25, respectively. None of these was identified as 3-phenyl-3-methylbutanoic, 2-phenyl-2-methylbutanoic, 2,2-dimethyl-3-phenylpropanoic, o-, m-, or p-t-butylbenzoic acid. The neutral product was analyzed directly in solution of diethyl ether and tetrahydrofuran by VPC and found to yield 5.19 g (0.0387 mole, 64.3 percent) of t-butylbenzene, 0.417 g (0.00311 mole, 6.16 percent) of i-butylbenzene and/or s-butylbenzene together with ca. 0.1 percent absolute yield of unreacted chloride.

Synthesis of Phenethyllithium

Into a 500 ml Morton flask equipped with a high-speed stirrer was distilled, from over sodium aluminum hydride, 250 ml of tetrahydrofuran. Lithium (1.95 g, 0.281 g atom) cut into small pieces was added to the flask and the temperature was lowered to -10°; methyl iodide (0.6 ml) and ca. 5 percent of a solution of 1-chloro-2-phenylethane (2.77 g, 0.0197 mole) in 10 ml of tetrahydrofuran was added. The mixture was stirred at -10 ± 2° for 40 minutes whereupon a light purple color started to develop; the temperature was lowered to -60° and stirring was continued at -60 ± 5° for 90 minutes. Since there was no appreciable color change, the tempera-

ture was raised to 0° and a solution of 0.0934 g of 1-chloro-2,2,2-triphenylethane in 0.5 ml of tetrahydrofuran was added to serve as an indicator for the initiation of the reaction; the solution was stirred at 0° for an additional 75 minutes. Again there was no observable color change. Then stirring was stopped and a solution of 0.206 g of 1-chloro-2,2,3-triphenylpropane (as indicator) in 1 ml of tetrahydrofuran was added at 0° and a deep red color developed immediately. The solution was cooled to -64° under vigorous stirring and the remaining chlorophenylethane solution was added dropwise over a period of four minutes; the resulting red solution was stirred at -65 ± 3° for two hours before carbonation. The carbonated product was worked up in the same manner as for the neophyllithium preparation to give 2.05 g (0.0136 mole, 69.3 percent yield based on the chloride used) of light yellow solid acidic material, m.p. 43-7°; a 1:1 mixture of this acid with an authentic sample of 3-phenylpropanoic acid (m.p. 47.5-9°) melts at 45-8°. The neutral material in ether solution was directly subjected to VPC analysis and found to contain, in the volatile fraction, mainly (> 94 percent) ethylbenzene (0.498 g, 0.00469 mole, 23.8 percent yield based on the chloride used).

Synthesis of 2-p-Biphenylylethyllithium

Into 250 ml of freshly distilled tetrahydrofuran was placed lithium metal (0.5908 g, 0.0851 g atom) in small pieces and the solution under vigorous stirring was cooled to -10°. Approximately five percent of a solution of 4.68 g (0.0216 mole) of 1-chloro-2-p-biphenylylethane in 25 ml of anhydrous tetrahydrofuran and 0.5 ml of methyl iodide were added to the solution, and stirring was continued at -10° for 15 minutes whereupon a

pink color started to appear. The pink color turned to green in another two minutes and this green color deepened with time. After a total of one hour of stirring at -15 ± 5°, the temperature was lowered to -70° and then to the greenish solution was added the remainder of the chloride dropwise over a period of 32 minutes. The first portion of chloride added caused the appearance of a pink color and the color deepened with stirring. The resulting reddish-brown solution was stirred at -70° for another 166 minutes whereupon a greenish color started to develop. The stirring was continued at -70° for another seven minutes before four 5 ml aliquots were withdrawn for Gilman titration. This titration indicated a yield of 18 percent of organolithium compound. The solution was stirred at -70° for an additional two hours and then syphoned into a flask containing a large excess of crushed solid carbon dioxide. The carbonated solution was allowed to stand overnight and about 100 ml of water was added to decompose unreacted lithium. Tetrahydrofuran was removed under partial vacuum and the residue was extracted with ether to yield 2.98 g (0.0164 mole, 75.7 percent yield) of semi-solid neutral material. The aqueous phase was acidified, extracted with ether giving 1.05 g (0.00463 mole, 21.4 percent yield based on chloride used) of solid acidic material, m.p. 94-121°. A sample of 0.901 g of this acidic material was sublimed at 150° and 80 to 100 microns pressure to give 0.332 g, m.p. 138-148° (premelting at 128°). A 0.0834 g sample of this acidic material was converted into 0.0878 g of methyl ester, m.p. 48-50°, by reacting with excess diazomethane. VPC analysis indicated that this was a pure methyl ester. The nmr spectrum showed 8.87 H at 2.58 to 3.00 τ (m, aromatic hydrogens), 3.00 H at 6.47 τ (s, methoxyl group), 2.12 H at 7.20 τ (unsym. t, J = 7 Hz, assigned to methylene group adjacent to the

aromatic ring), and 2.12 H at 7.44 τ (unsym. t, J = 7 Hz, methylene group adjacent to the carboxyl group). This nmr indicated that it was essentially pure methyl 3-p-biphenylylpropanoate. VPC of a small portion of the neutral product showed there were three compounds in yields of 1.08 g (0.00591 mole, 27.3 percent) of ethylbiphenyl (retention time 2.3 minutes), 3.46 area percent of an unknown of retention time 7.8 minutes, and 0.55 area percent of another unknown of retention time 9.0 minutes. The VPC retention time of the starting chloride under the same conditions was 6.7 minutes; this component was absent in the neutral material.

In run 2, the reaction of 4.89 g (0.0226 mole) of 1-chloro-2-p-biphenylylethane with lithium (1.24 g, 0.179 g atom) was initiated at -10° in the same manner as in the first run. The temperature was then lowered to -70° and the chloride was added at this temperature over a period of 20 minutes. The red solution was stirred at -70° for another 38 minutes before samples were withdrawn for Gilman titration.[35] This titration indicated a yield of 49.5 percent of organolithium compound. After the withdrawal of samples, an aliquot of 100 ml of the reddish brown solution was carbonated (fraction 1). The remainder of the solution was stirred at -67 ± 2° for another 20 minutes, where a greenish color appeared, and the stirring was continued at -67 ± 2° for one additional hour; samples were again withdrawn for Gilman titration and the remainder was carbonated (fraction 2). This last titration indicated a yield of 96.3 percent. A usual work-up gave in the first fraction 0.851 g of white crystalline acidic material, m.p. 146-51° (with residue) and 1.48 g of semi-solid neutral material, and in the second fraction 1.42 g of pale yellow solid acidic material, m.p. 128-146° and 1.21 g of semi-solid neutral material. A 0.856 g sample of

the acidic product from fraction 1 was sublimed at 130° and 60 microns pressure giving 0.689 g (0.00304 mole, 33.7 percent yield based on the halide used) of sublimate, m.p. 150-2° (premelting at 145°). A 0.109 g sample of this acidic material was reacted with diazomethane yielding 0.112 g of methyl ester, m.p. 56-7°. VPC of this methyl ester showed that it was a pure compound. The nmr spectrum showed 9.07 H at 2.58-3.00 τ (m, aromatic hydrogens), 3.00 H at 6.47 τ (s, methoxyl group), 2.12 H at 7.20 τ (unsym. t, J = 7 Hz, methylene group adjacent to the aromatic ring), and 2.12 H at 7.44 τ (unsym. t, J = 7 Hz, methylene group adjacent to the carboxyl group). A 1.42 g sample of the acidic product from fraction 2 was also sublimed at 130° and 60 microns giving 0.840 g (0.00371 mole, 27.5 percent yield based on the halide used) of sublimate, m.p. 147-50.5° (premelting at 138°). A 0.120 g sample of this acidic material was converted into 0.126 g of methyl ester, m.p. 54-7°, by reacting with diazomethane. VPC showed only a single peak and the nmr spectrum of this methyl ester showed 9.23 H at 2.58 to 3.00 τ (m, aromatic hydrogens), 3.00 H at 6.47 τ (s, methoxyl group), 2.07 H at 7.20 τ (unsym. t, J = 7 Hz, methylene group adjacent to the aromatic ring), and 2.07 H at 7.44 τ (unsym. t, J = 7 Hz, methylene group adjacent to the carboxyl group). This spectrum indicated that this ester is essentially pure methyl 3-p-biphenylylpropanoate.

VPC of the neutral product showed that there were three compounds with retention times 2.3 minutes, 7.8 minutes, and 9.0 minutes in ratios of 63.9 : 9.8 : 26.3 in fraction 1 and there were two compounds with retention times of 2.3 minutes and 9.0 minutes in a ratio of 81.73 to 18.27 in fraction 2. The 2.3 minutes peak was identified as ethylbiphenyl.

In run 3, the reaction of 4.98 g (0.0230 mole) of 1-chloro-2-p-

biphenylylethane with slightly excess lithium (0.3740 g, 0.0539 g atom) was initiated in the usual manner at -8°. The temperature was then lowered to -70° and the chloride in 37 ml of anhydrous tetrahydrofuran was added dropwise over a period of 30 minutes at -72 ± 2°. The first portion of chloride added caused the appearance of a pink color which developed through yellow to purple throughout the addition. The stirring was continued at -73° for 100 minutes and an aliquot of 100 ml of the purple colored solution was carbonated (fraction 1). The remainder of the solution was stirred at -73° for an additional 40 minutes before carbonation (fraction 2). The solution before carbonation was purple. A usual work-up yielded in the first fraction 0.0867 g of acidic material and 2.22 g of neutral material; in the second fraction 0.0850 g of acidic material and 2.15 g of neutral material. Vapor phase chromatography of the neutral products is given in Table 9. VPC of the methyl esters produced 0.0361 g (0.000160 mole, 1.53 percent) and 0.0599 g (0.000265 mole, 2.56 percent), respectively, of 3-p-biphenylylpropanoic acid in fractions 1 and 2.

In run 4, the reaction of 5.01 g (0.0231 mole) of 1-chloro-2-p-biphenylylethane with a large excess of lithium (2.55 g, 0.367 g atom) was initiated at -10° by adding 1 ml of methyl iodide and ca. 4 percent of the halide solution in 35 ml of tetrahydrofuran to the reaction vessel; the solution was stirred at -10 ± 5° for one hour. The final color of the solution after this initiation period was green. The temperature was then lowered to -74° and the remainder of the halide was added dropwise over a period of 20 minutes. The first portion of halide added caused the appearance of a pink color, which deepened to brown at the end of addition. The solution was stirred at -73° for another 10 minutes, when a green color

Table 9. Vapor-Phase Chromatographic Analyses of Neutral Products in the Synthesis of 2-p-Biphenylylethyllithium (Run 3)

Retention Time min	(Relative Retention Time)	Area Percent (Absolute Yield Percent)		Identification
		Fraction 1	Fraction 2	
2.7	(1.00)	13.76 (10.68)	25.35 (17.91)	p-Ethylbiphenyl
3.1	(1.15)	1.68 (1.30)	1.04 (0.73)	p-Vinylbiphenyl
7.7	(2.85)	83.56 (54.38)	70.14 (41.59)	Unreacted Chloride
10.6	(3.93)	1.00 (0.65)	3.47 (2.06)	

VPC conditions used: temperature 157°; flow rate 25 mm; pressure 60 psig.

started to develop. This green colored solution was immediately carbonated. A usual work-up gave 2.73 g (0.0121 mole, 52.2 percent yield) of acidic material, m.p. 146-150.5°, and 3.08 g of semi-solid neutral material. A 2.72 g sample of the crude acidic product was vacuum sublimed at 135° at 60 microns yielding 2.50 g (91.9 percent volatile) of white crystals, m.p. 150-1.5°. One recrystallization of 2.13 g of this acidic material from ethanol gave 1.53 g, m.p. 150-151.5°. A small sample of this acid was analyzed for C, H content.

Anal.* Found: C, 79.81, 79.95; H, 5.94, 6.14. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24.

Another sample of 0.341 g was converted into methyl ester (0.374 g, m.p. 56.5-7.5°) by reacting with excess diazomethane. A sample of this methyl ester (p-$PhC_6H_4CH_2CH_2CO_2Me$) was vacuum sublimed at 80° and 30 microns, recrystallized from methanol, and again sublimed at 93° and 30 microns to give an analytical sample, m.p. 57.5-58.3°.

Anal.* Found: C, 80.14, 80.08; H, 6.70, 6.71. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71.

The nmr spectrum of this methyl ester showed 9.04 H at 2.50 to 3.00 τ (m, aromatic hydrogens), 3.00 H at 6.50 τ (s, methoxyl group), 1.98 H centered at 7.17 τ (unsym. t, methylene group adjacent to the aromatic ring), and 1.98 H at 7.54 τ (unsy. t, methylene group adjacent to the carboxyl group). This nmr further confirmed that this ester was methyl 3-p-biphenylylpropanoate. The neutral product was subjected to VPC analysis and found to contain only one single volatile material in absolute yield of 9.66 percent which was doubtlessly ethylbiphenyl.

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*Analysis by Galbraith Laboratories, Inc., Knoxville, Tennessee.

In run 5, the reaction of 5.01 g (0.231 mole) of 1-chloro-2-p-biphenylylethane with lithium (2.50 g, 0.36 g atom) was initiated in the same way as in previous runs. Then the temperature was lowered to -74° in 10 minutes and the chloride in 40 ml of tetrahydrofuran was added at -73° dropwise over a period of 14 minutes. The resulting reddish-brown solution was stirred at -73° for another six minutes (the solution was still reddish brown) and four aliquots of 5 ml samples were withdrawn for Gilman titration and the remainder was filtered through a siphon tube packed loosely with a small amount of glass wool into a 500-ml, three-necked, round-bottomed flask under N_2. This titration did not show any informative result apparently due to the large excess of lithium. The filtered solution was kept at Dry Ice-acetone bath temperature for five minutes and another four aliquots of 5 ml samples were withdrawn for Gilman titration. After one more hour of standing at Dry Ice-acetone bath temperature, another four aliquots of 5 ml samples were again withdrawn for Gilman titration, and an aliquot of 100 ml of the solution was carbonated (fraction 1). These last two titrations again failed to give any useful information about the yields of organolithium compounds, apparently because the benzyl chloride sample used to react with organolithium compounds was no longer effective. The remainder of the solution was allowed to stand at Dry Ice-acetone temperature for a total of four hours (from the time the filtration was completed) before carbonation (fraction 2). A usual work-up yielded in the first fraction 0.629 g (0.00278 mole, 26.5 percent yield) of solid acidic material, m.p. 148-150.5°, and 1.38 g (0.00758 mole, 72.2 percent) of semi-solid neutral material and in the second fraction 0.483 g (0.00125 mole, 20.4 percent yield) of acidic material, m.p. 148-150.5°, and 0.760 g

(0.00418 mole, 68.2 percent) of neutral material. VPC of the neutral material is given in Table 10.

Table 10. VPC Analyses of Neutral Products in the Syntheses of 2-p-Biphenylylethyllithium (Runs 5 and 6)

Retention Time min	(Relative Retention Time)	Area Percent (Abs. Yield %) Run 5 Fract. 1	Area Percent (Abs. Yield %) Run 5 Fract. 2	Area Percent (Abs. Yield %) Run 6	Identification
3.7	(1.00)	50.00 (12.81)	53.66 (10.80)	95.60 (24.39)	p-Ethylbiphenyl
4.2	(1.13)			1.10 (0.28)	p-Vinylbiphenyl
11.1	(3.00)*	36.27 (7.80)	21.95 (3.71)		
12.0	(3.24)	13.73 (2.95)	24.39 (4.12)		
14.0	(3.78)			1.10 (0.28)	
15.0	(4.05)			0.55 (0.14)	
16.6	(4.49)			1.65 (0.42)	

*1-Chloro-2-p-biphenylylethane has a relative retention time of 3.09, hence could possibly be covered under this peak.

VPC conditions used: temperature 150°; flow rate 22 mm; pressure 60 psig.

In run 6, the reaction of 5.01 g (0.0231 mole) of 1-chloro-2-p-

biphenylylethane with lithium (2.55 g, 0.367 g atom) was initiated in the same manner as in the previous run. Then the temperature was lowered to -75° and the greenish solution was stirred at -75 ± 1° for one hour. The halide in 25 ml of anhydrous tetrahydrofuran was added at -76° dropwise over a period of 22 minutes. A brownish-red color developed in the first minute of the addition. The stirring was continued at -75° for 28 minutes when a greenish color started to develop. The solution was then filtered through a siphon tube packed at the end loosely with a small amount of glass wool into a 500-ml, round-bottomed, three-necked flask under nitrogen atmosphere. The solution at -30° was greenish with slight red and was gradually warmed up to 0.5° in 17 minutes and kept at 0 ± 3° for one hour before carbonation. The solution before carbonation was reddish brown. The carbonated product was allowed to stand overnight and to it was then added 100 ml of water and THF was removed under partial vacuum. The residue was then acidified and extracted with four 100 ml portions of ether. The ethereal extracts were combined, washed with three 100 ml portions of water, extracted with a solution of sodium thiosulfate (2 g $Na_2S_2O_3$ in 100 ml H_2O, 1 g NaI, and 1 ml acetic acid), again washed with two 100 ml portions of water. This ether solution was extracted with three 100 ml portions of six percent $NaHCO_3$, washed with water, dried over $MgSO_4$, and filtered. After evaporating ether, there was obtained 2.86 g (0.0157 mole, 67.9 percent yield) of semi-solid neutral material. The $NaHCO_3$ extracts and washing solutions were combined, acidified, and extracted with three 100 ml portions of ether. This ethereal solution was washed with water, dried over anhydrous $MgSO_4$, filtered, and solvent evaporated to give 1.97 g (0.00872 mole, 37.7 percent yield) of acidic material, m.p. 145-150° (with residue). A sample

of 0.214 g of this crude acidic product was converted into 0.226 g (99.1 percent yield based on the acid used) of methyl ester, m.p. 54.5-57°, which was sublimed at 90° and 100 microns yielding 0.197 g (0.000819 mole, 89.3 percent) of white crystalline ester, m.p. 53.5-57° (with premelting). A small portion of the neutral product was subjected to VPC analysis (see Table 10). A 2.41 g sample of this neutral product was sublimed three times at 50° and 50 microns giving 0.323 g of colorless crystalline material, m.p. 34-35.5° (reported[36] m.p. of p-biphenylylethane: 32-34°). The nmr spectrum of this hydrocarbon [a multiplet centered at 2.83 τ (9.00 H); a triplet at 7.49 τ (J = 7.5 Hz, 1.89 H); a quartet at 8.87 τ (J = 7.5 Hz, 3.04 H)] confirmed the structure of p-biphenylylethane.

Reaction of 1-Chloro-2-p-biphenylylethane-1,1-d_2 with Lithium

The reaction was carried out in the same kind of apparatus as in the reaction of 1-chloro-2-p-biphenylylethane. Into 250 ml of freshly distilled tetrahydrofuran was placed 2.17 g (0.313 g atom) of lithium (0.05 percent sodium max.) cut into small pieces and 1 ml of methyl iodide. The solution was cooled under vigorous stirring to -9° and a small portion (20 drops) of a solution of 5.01 g (0.0221 mole) of 1-chloro-2-p-biphenylylethane-1,1-d_2 in 25 ml of anhydrous tetrahydrofuran was added. A pale pink color appeared in the first 30 seconds, which turned into reddish brown and finally into green in five minutes. The solution was stirred at -10 ± 3° for one hour and then the temperature was lowered to -74°. The stirring was continued at -70 ± 5° for 30 minutes and then the remainder of the halide

(36) A. Rembaum, A. Eisenberg, R. Haack, and R. F. Landel, J. Am. Chem. Soc., 89, 1062 (1967).

was added dropwise over a period of 17 minutes. The first portion of halide added caused the reappearance of a light reddish brown color which deepened throughout addition. The reddish brown solution was stirred at -73 ± 2° for another 16 minutes when a greenish color started to develop. The greenish solution was immediately carbonated. After standing at room temperature for four hours, the product was worked up in the same manner as in the last run of the previous section yielding 3.51 g (0.0154 mole, 69.3 percent yield based on the chloride used) of light yellowish crystalline acidic material, m.p. 146-150° with residue, and 2.41 g of semi-solid neutral material. A sample of 0.639 g of the acidic material was converted into 0.664 g of methyl ester, m.p. 53-56.3° with residue, which was vacuum sublimed at 95° and 30 microns yielding 0.576 g (90.6 percent based on crude acid used) of white crystalline material, m.p. 53-57.7°. The nmr spectrum [a multiplet centered at 2.70 τ (9.00 H), aromatic hydrogens; a singlet at 6.41 τ (3.01 H), methoxyl group; and a singlet at 7.10 τ (2.01 H), methylene group adjacent to the aromatic ring] indicated that it was pure methyl 3-p-biphenylylpropanoate-2,2-d_2. The neutral material was analyzed by VPC and found to yield 0.30 g (constituted 94 percent of the volatile hydrocarbons) of p-biphenylylethane-d_2 together with three others in yields (relative retention time, based on p-biphenylylethane-2,2-d_2 as standard) of 0.0074 g (3.86), 0.0030 g (4.14), and 0.0096 g (4.57). No further effort was made in the purification and identification of the neutral product.

In run 2, the reaction of 4.66 g (0.0213 mole) of 1-chloro-2-p-biphenylylethane-1,1-d_2 with lithium (2.18 g, 0.314 g atom) was initiated in the same manner as in run 1, and then the temperature was lowered to

-68° and the solution was stirred at -68 ± 2° for one hour. The remainder of the halide was added at -68° dropwise over a period of 15 minutes. A reddish brown color appeared in the first minute of this addition. The reddish brown solution was stirred at -68° for 15 minutes until a greenish color started to develop. This predominantly greenish solution was transferred through a siphon tube packed loosely with a small amount of glass wool at the end into a 500 ml three-necked, round-bottomed flask cooled in an ice-bath under nitrogen atmosphere. The solution was kept under a nitrogen atmosphere at 0 ± 3° for 170 minutes and then carbonated. The color of the solution before carbonation had changed from green to black during the first hour of standing and then gradually to slightly reddish in the next 20 minutes; the final color was reddish brown. The carbonated product was worked up in the same manner as in the previous run, except that a solution of 2 percent KOH was used instead of 6 percent $NaHCO_3$ for the extraction of the original ethereal solution, giving 2.22 g (0.00975 mole, 45.7 percent yield) of acidic material, m.p. 137-146° with premelting around 125°, and 2.52 g of neutral material. A sample of 0.150 g of the acidic material was converted into 0.157 g of methyl ester. A 0.154 g sample of the latter was sublimed at 85° at 50 microns pressure to give 0.119 g, m.p. 50.5-57° (premelting at 44°). The nmr spectrum of this ester showed 9.00 H centered at 2.70 τ (m, aromatic hydrogens), 3.04 H at 6.41 τ (s, methoxyl group), 1.90 H at 7.10 τ (s, methylene group adjacent to the aromatic ring), and ca. 0.08 H at 7.45 τ (methylene group adjacent to the carboxyl group). A sample of the neutral material was subjected to VPC analysis and found to contain in the volatile fraction 98.6 percent (by VPC area) of p-biphenylylethane-d_2 (the absolute yield was 42.6 percent

based on chloride used), 0.57 percent of a compound of relative retention time 1.13 (based on retention time of p-biphenylylethane), and 0.81 percent of another compound of relative retention time 4.43.

In run 3, 1-chloro-2-p-biphenylylethane-1,1-d_2 (4.51 g, 0.0206 mole) was reacted with lithium (2.20 g, 0.317 g atom) at -73° in tetrahydrofuran in the usual manner for 26 minutes (15 minutes addition and 11 minutes stirring before the appearance of a green color) and then the solution was filtered in the same way as in the previous run into a 500 ml three-necked, round-bottomed flask under nitrogen atmosphere. The greenish solution at -29° was warmed up to 0° in 18 minutes in an ice-bath and then allowed to stand at 2.5 ± 1° for 16½ hours before carbonation. A black color started to develop in the first one and one-half hours of standing, which gradually turned to reddish brown and the final color before carbonation was like that of $KMnO_4$. A usual work-up yielded 0.842 g of oily acidic material and 3.45 g of semi-solid neutral material. The acidic material was reacted with diazomethane and then a 0.772 g sample was sublimed at 105° and 90 microns to give 0.256 g of semi-solid material. VPC and nmr of this sample showed that it contained quite a big fraction of neutral material (ratio of p-biphenylylethane to esters was 6 to 1) apparently due to the incompleteness of separation during work-up. The neutral material was vacuum sublimed three times at 100° and 70 microns giving some 1.67 g of semi-solid material. One recrystallization from pentane gave 0.101 g of white crystalline material, m.p. 31-3° (premelts at 26°). VPC and nmr* [a multiplet centered at 2.83 τ (9.00 H), aromatic hydrogens; a doublet centered at 7.52 τ

*TMS was used as external standard.

(1.86 H, J = 8 Hz), methylene group adjacent to the aromatic ring; a triplet centered at 8.93 τ (1.16 H, J = 7.5 Hz), methyl group] of this low melting hydrocarbon indicated that it was predominantly p-biphenylylethane-2, 2-d_2 contaminated by no more than 7.5 percent of p-biphenylylethane-1,1-d_2.

In run 4, 1-chloro-2-p-biphenylylethane-1,1-d_2 (5.02 g, 0.0229 mole) was reacted with lithium (2.54 g, 0.366 g atom) in tetrahydrofuran at -71° in the usual manner for 23 minutes (20 minutes addition and three minutes stirring before the reappearance of a green color). The color of the solution remains green throughout the addition until the last minute when a brown color started to develop. The quickness of the reappearance of the green color was apparently due to the very finely divided metal particles. The green solution was transferred using the same technique as used in previous runs into a 500-ml, three-necked, round-bottomed flask under nitrogen atmosphere. The vessel containing the solution at -3° was sealed against the atmosphere with well greased glass stoppers and kept at 1.0 ± 1° for nine hours giving a reddish brown solution. This reddish brown solution was then carbonated. The carbonated product was allowed to stand at room temperature for four hours and to it was added 100 ml of water; tetrahydrofuran was removed under partial vacuum. The residue was acidified, extracted with four 80 ml portions of ether, and the ethereal extract was combined, washed with 100 ml of water, a solution of sodium thiosulfate (2 g $Na_2S_2O_3$, 1 g of NaI, 1 ml HOAC, and 100 ml water), and three 80 ml portions of water. This ethereal solution was then extracted with three 80 ml portions of 2 percent KOH, washed twice with water, dried over $MgSO_4$, and filtered. After evaporating ether, there was obtained 3.83

grams (0.0208 mole, 90.9 percent yield) of semi-solid neutral material. The aqueous phases were combined, washed twice with ether, acidified, and extracted with three 100 ml portions of ether. The ethereal extracts were combined, washed twice with water, dried over $MgSO_4$, filtered, and solvent evaporated giving 0.915 g (0.00403 mole, 17.5 percent yield) of semi-solid acidic material. A 0.914 g sample of this crude acidic material was reacted with diazomethane yielding 0.849 g (0.00351 mole, 87.5 percent based on acid used) of methyl ester. A 0.778 g sample of this methyl ester was sublimed twice at 85° at 30 microns to give 0.595 g (66.9 percent yield based on the acidic material used), m.p. 54-7.5°. VPC of this sublimate showed that there were four volatile esters among which methyl 3-p-biphenylylpropanoate-2,2-d_2 was obtained in 7.41 percent yield (constituted 66.5 percent of the total volatile fraction), and the remaining three esters obtained in yields (relative retention time, based on methyl 3-p-biphenylylpropanoate-d_2) of 0.09 percent (0.68), 1.05 percent (0.76), and 2.59 percent (1.44) were not identified. One recrystallization of this ester mixture from pentane gave 0.216 g of a white flaky crystal, m.p. 56.5-7.5°. VPC of which showed only one single peak, and the nmr spectrum [a multiplet centered at 2.70 τ (9.66 H), aromatic hydrogens; a singlet at 6.41 τ (3.00 H), methoxyl group, a singlet at 7.10 τ (2.00 H), methylene group adjacent to the aromatic ring] indicated that this sample was methyl 2-p-biphenylylpropanoate-2,2-d_2 within experimental error. A sample of the crude neutral product was subjected to VPC analysis and found to contain, in the volatile portion, 96.0 percent of p-biphenylylethane-d_2 together with four others in relative amount (relative retention time, based on p-biphenylylethane-d_2) of 0.38 percent (1.85), 1.44 percent (2.23), 1.63 percent (3.54), and

0.58 percent (4.04). A 3.28 g sample of this crude neutral material was sublimed twice at 65° at 100 microns pressure giving 1.85 g (51.6 percent yield based on the chloride used) of a solid, m.p. 32-3°. The nuclear magnetic resonance spectrum [a multiplet centered at 2.85 τ (9.00 H), aromatic hydrogens; a doublet centered at 7.49 τ (1.92 H), methylene group adjacent to the aromatic ring; a triplet centered at 8.91 τ (1.13 H), methyl group] showed that it was predominantly p-biphenylylethane-2,2-d_2 contaminated by less than 5.3 percent of p-biphenylylethane-1,1-d_2.

In run 5, the reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 (2.01 g, 0.00918 mole) with lithium (0.960 g, 0.138 g atom) in tetrahydrofuran was initiated in the usual manner at -10°. Then the temperature was lowered to -65° and the balance of the halide solution together with 3.94 g (0.0340 mole) of N,N,N',N'-tetramethylethylenediamine (TMEDA) was added dropwise over a period of 25 minutes. The first portion of halide added caused the development of a pink color and the color near the end of the addition was reddish purple. The resulting reddish purple solution was stirred at -65° for 10 minutes and then filtered through a siphon tube packed at one end loosely with glass wool into a 500-ml, three-necked, round-bottomed flask. This flask containing the reddish purple solution of organolithium compound was allowed to stand at 4° for one hour with occasional shaking by hand and then carbonated. The solution before carbonation was reddish brown. The next day, water was added to the solution to decompose the unreacted lithium and the resulting solution was acidified. THF was removed under partial vacuum and the residue was extracted four times with a total of 500 ml of ether. The ethereal extracts were combined, washed with water, extracted with a 3 percent KOH solution, washed again with

water, and dried over anhydrous $MgSO_4$. After removing ether under partial vacuum, neutral material was obtained in an amount of 1.74 g (0.00946 mole) as a light yellow wet oil. The alkaline solution was acidified, extracted with three 100 ml portions of ether, and the ethereal extracts were combined, washed with water, dried over $MgSO_4$, and filtered. After removing the ether, there was obtained 0.278 g (0.00122 mole, 13.3 percent) of a light yellow acidic material, m.p. 140-150°. This acidic material was reacted with diazomethane to give 0.299 g of methyl ester, m.p. 45-54°, with unmelted residue. A 0.244 g sample of this crude ester was sublimed twice at 72 to 90° at 60 microns pressure to give 0.173 g of white solid, m.p. 52-5°. The nmr spectrum [a multiplet centered at 2.70 τ (9.00 H), aromatic hydrogens; a singlet at 6.41 τ (2.97 H), methoxyl group; and a singlet at 7.10 τ (1.89 H), methylene group adjacent to the aromatic ring] indicated that it was methyl 3-p-biphenylylpropanoate-2,2-d_2 containing no rearranged methyl ester within experimental error (6 percent). The crude neutral product above was analyzed by VPC and found to contain 0.622 g (0.00338 mole, 36.8 percent yield) of p-biphenylylethane-d_2, no unreacted chloride, and the remainder non-volatile compounds. A 1.60 g sample of this crude neutral product was sublimed twice at 52° and 70 microns pressure to give 0.529 g of a transparent crystalline material, m.p. 28-31°. A small sample of this crystalline material was sublimed the third time and then analyzed by the nmr. This analysis showed that it was p-biphenylylethane-2,2-d_2 contaminated by less than 7.1 percent ± 3 percent (if at all) of p-biphenylylethane-1,1-d_2.

Reaction of 1-Chloro-2-p-biphenylylethane with Cesium and Cs-K-Na Alloy

In run 1, liquid cesium-potassium-sodium alloy was prepared in the usual apparatus from 5.18 g (0.0390 g atom) of cesium, 1.71 g (0.0438 g atom) of potassium, and 0.213 g (0.00926 g atom) of sodium in 250 ml of tetrahydrofuran, heated at reflux with stirring. The color of the solution changed from blue to green and finally to brown during stirring. After stirring at reflux for one hour, the mixture was cooled to -70° and a solution of 0.967 g (0.00446 mole) of 1-chloro-2-p-biphenylylethane in 25 ml of dry tetrahydrofuran was added dropwise over a period of three minutes. The first portion of the halide added caused the development of a bright red color. Stirring was continued at -78° for another three minutes, whereupon a brown color started to develop and the solution became viscous; this solution was immediately carbonated. A usual work-up yielded 0.679 g of brownish solid acidic material, m.p. > 203° with decomposition, and 0.893 g of greenish oily neutral material. VPC of the neutral material showed that p-biphenylylethane was the only volatile neutral product contaminated by less than one percent of a lower molecular weight compound. A 0.790 g sample of this neutral material was sublimed at 65° and 80 microns pressure to give 0.0591 g of light brown liquid. VPC of the acidic product (as methyl esters) showed only two compounds; the absolute yield of each was 0.013 g (1.26 percent based on the halide used). One of them was identified as methyl 3-p-biphenylylpropanoate, and the other one with a relative retention time of 0.75 (based on methyl 3-p-biphenylylpropanoate) was unidentified.

In run 2, liquid cesium-potassium-sodium alloy was prepared in the

same manner as in run 1 from 5.47 g (0.0411 g atom) of cesium, 1.68 g (0.0431 g atom) of potassium, and 0.205 g (0.0089 g atom) of sodium in 250 ml of tetrahydrofuran. The temperature was then lowered to -67° and stirring was continued at -67° for 30 minutes. A solution of 1.01 g (0.00466 mole) of the chloride in 25 ml of dry tetrahydrofuran was added dropwise over a period of eight and one-half minutes and stirring was continued at -64° for one additional minute; then the brownish solution was carbonated. A usual work-up gave 1.13 g of acidic material, m.p. 170-210° with premelting and decomposition, and 0.462 g of brownish tarry neutral material. The neutral material was subjected to VPC analysis and was found to contain 0.000327 g of p-biphenylylethane together with 0.00273 g of a compound of shorter retention time (relative retention time 0.76 based on p-biphenylylethane). VPC of the acidic material (as methyl esters) showed that there were a total of nine compounds obtained in an overall yield of 0.250 g (0.00104 mole, 22.3 percent). Among these methyl 3-p-biphenylylpropanoate was obtained in only 0.0054 g (2.25×10^{-5} mole, 0.482 percent based on the halide used).

In run 3, cesium-potassium-sodium alloy (0.58 ml, ca. 0.011 g atom), previously prepared from 5.00 g of cesium, 1.67 g of potassium, and 0.186 g of sodium, was placed in 250 ml of freshly distilled tetrahydrofuran. The solution was stirred at reflux for one hour and then cooled to -63° giving a greenish solution. A solution of 1.02 g (0.00471 mole) of the chloride in 25 ml of dry THF was added dropwise over a period of 37 minutes and stirring was continued at -63° for another five minutes before carbonation. The first portion of the halide added caused a red color to appear in the solution and the final color was reddish brown. A usual

work-up yielded 1.10 g of light brownish tarry neutral material and 0.382 g of brownish tarry acidic material. A 0.932 g sample of the neutral material was sublimed at 80° and 50 microns pressure to give 0.352 g (0.00193 mole, 41.0 percent yield based on the halide used) of light yellow liquid; vapor-phase chromatography showed only a single peak identified by comparison of retention time as p-biphenylylethane (0.278 g, 32.4 percent yield based on the halide used). The nmr spectrum [a multiplet centered at 2.84 τ (9.00 H), aromatic hydrogens; a quartet centered at 7.51 τ (2.08 H); methylene group adjacent to the aromatic ring; and a triplet on top of a multiplet at 8.92 τ (ca. 6.5 H), methyl group] indicated that it was p-biphenylylethane contaminated by impurities apparently from the lubricant. VPC of the acidic material (as methyl esters) showed the presence of seven volatile compounds in an overall yield of 0.00886 g, which contained 0.00334 g of methyl 3-pbiphenylylpropanote.

In run 4, cesium (3.47 g, 0.0261 g atom) was placed in 250 ml of freshly distilled tetrahydrofuran and the mixture was stirred at reflux for 30 minutes giving a dark green solution with finely divided metal particles. Then, a solution of 2.46 g (0.0114 mole) of 1-chloro-2-p-biphenylylethane in 25 ml of anhydrous tetrahydrofuran was added dropwise over a period of 20 minutes. The resulting reddish brown solution was stirred at reflux for five minutes and then cooled at room temperature without stirring for 10 minutes before carbonation. A usual work-up yielded 1.38 g of neutral material and 1.43 g of solid acidic material, m.p. 118-320° with decomposition. VPC of the crude neutral product yielded 0.369 g (0.00202 mole, 17.8 percent yield based on the halide used) of p-biphenylylethane which constituted 95.1 percent of the volatile hydrocarbons [there were two unidentified

compounds with area percent (relative retention time, based on p-biphenylylethane) of 2.8 (0.676) and 2.1 (4.60)]. A 1.23 g sample of the crude neutral material was sublimed at 70° at 60 microns pressure to give 0.314 g of an amber semi-solid, which after one recrystallization from pentane gave 0.0612 g of a colorless crystalline material. This crystalline material melted at room temperature and the nmr spectrum [a multiplet at 2.83 τ (9.0 H), aromatic hydrogens; a quartet centered at 7.47 τ (2.0 H), methylene group adjacent to the aromatic ring; and a triplet on top of a multiplet at 8.87 τ (ca. 3.6 H)] indicated that it was p-biphenylylethane contaminated by some impurities apparently from the lubricant.

Reaction of 1-Chloro-2-p-biphenylylethane-1,1-d_2 with Cesium and Cs-K-Na Alloy

Into 300 ml of freshly distilled tetrahydrofuran was placed 0.55 ml (ca. 0.0107 g atom) of cesium-potassium-sodium alloy prepared from 23.8 g of cesium, 7.96 g of potassium, and 0.880 g of sodium. The mixture was stirred at reflux for one hour and then cooled to -65°, followed by stirring for 30 minutes at -65 ± 3°. A solution of 0.982 g (0.00449 mole) 1-chloro-2-p-biphenylylethane-1,1-d_2 in 25 ml of dry THF was added dropwise over a period of 40 minutes and stirring was continued at -66 ± 2° for an additional five minutes before carbonation. The first portion of the halide added caused the development of a black-brown color in the solution and the final color before carbonation was reddish brown. A usual work-up yielded 1.32 g of greenish-black tarry neutral material and 0.202 g of light brown tarry acidic material. VPC of the neutral material showed that it contained 0.230 g (27.8 percent yield based on the halide used) of p-

biphenylylethane-d_2, 0.0238 g (2.91 percent yield) of p-biphenylylethene-d_2, together with 0.100 g (10.3 percent yield) of unreacted chloride. A 1.20 g sample of this crude product was sublimed twice at 60° and 80 microns pressure to give 0.261 g of a semi-solid. The nmr of this sample showed that it contained the three compounds identified by VPC above together with some impurities apparently from the lubricant. VPC of the acidic product (as methyl esters) showed that it contained at least 10 compounds in an overall yield of only 0.00905 g (0.83 percent based on the halide used) and among these methyl 3-p-biphenylylpropanoate-d_2 was obtained in only 0.00119 g.

In run 2, into 250 ml of freshly distilled tetrahydrofuran was placed 0.827 g (0.0104 g atom) of the same cesium alloy used in run 1 and the solution was stirred at reflux for 30 minutes giving blue color which eventually became brown. The temperature was then lowered to -65°; the resulting green solution stirred at -65 ± 2° for 40 minutes, and a solution of 0.954 g (0.00436 mole) of the halide in 25 ml of anhydrous tetrahydrofuran was added dropwise over a period of 30 minutes. The first portion of halide added caused the appearance of a bright red color in the solution and the final color was deep red. This red solution was stirred at -65° for five minutes before carbonation. A usual work-up yielded 0.107 g of a semi-solid acidic material and 1.10 g of a yellow tarry neutral material. VPC of this crude neutral material produced p-biphenylylethane-d_2, p-biphenylylethene-d_2, and the unreacted chloride in yields (based on the starting halide used) of 20.8 percent (0.167 g, 0.000906 mole), 3.71 percent (0.0294 g, 0.000161 mole), and 8.67 percent (0.0827 g, 0.000378 mole), respectively. A 0.900 g sample was sublimed twice at 70° and 20 microns pressure yielding 0.227 g of a light yellow semi-solid sublimate. The nmr analysis showed

that it contained all of the three compounds identified by VPC above together with some impurities apparently from the lubricant. An attempted recrystallization failed to give any pure sample for nmr analysis.

In run 3, into 250 ml of freshly distilled tetrahydrofuran was placed 1.67 g (0.0215 g atom) of thoroughly washed (with pentane and tetrahydrofuran) cesium alloy and the solution was stirred at reflux for 30 minutes. The resulting greenish solution which turned blue again after cooling to -65° was stirred at -65° for 30 minutes, then a solution of 1.53 g (0.00699 mole) of the halide in 25 ml of anhydrous tetrahydrofuran was added dropwise over a period of 30 minutes whereupon the original cherry red color turned black brown. This black brown solution was stirred at -65° for five minutes and then carbonated. The product was worked up in the usual manner to give 0.805 g of light brownish oily neutral material and 0.952 g of a yellowish acidic material. VPC analysis of the crude neutral material produced 0.317 g (0.00172 mole, 24.6 percent yield based on the halide used) p-biphenylylethane-d_2 contaminated by less than one percent of impurity if any. A 0.742 g sample of this neutral material was sublimed twice at 65° at 50 microns pressure to give 0.268 g of a light blue crystalline solid, m.p. 29-32° (premelts ~ 26°), one recrystallization of which from pentane gave 0.113 g of a white solid, m.p. 33-33.6°. The nmr spectrum [a multiplet at 2.74 τ (9.00 H), aromatic hydrogens; a doublet centered at 7.42 τ (1.56 H); methylene group; and a singlet on top of a triplet at 8.81 τ (1.45 H), methyl group] indicated that it contained 77.7 percent of p-biphenylylethane-2,2-d_2 and 22.3 percent of p-biphenylylethane-1,1-d_2. VPC of the acidic material (as methyl esters) showed that it contained six compounds in an overall yield of 0.0153 g (6.33×10^{-5} mole,

0.91 percent yield based on the halide used).

In run 4, a solution of 2.35 g (0.0177 g atom) of cesium in 250 ml of freshly distilled tetrahydrofuran was stirred at 35° for one hour and then the chloride (1.29 g, 0.00589 mole) in 25 ml of tetrahydrofuran was added dropwise over a period of 15 minutes at 36 ± 2°. The first portion of halide added caused the appearance of a red color in the solution and the color changed through brownish into black throughout the addition. Stirring was continued at 38° for one minute before carbonation. A usual work-up gave 0.376 g of a light brownish semi-solid neutral material and 1.17 g of a light yellow semi-solid acidic material. VPC of the crude neutral material yielded 0.0601 g (0.000327 mole, 5.55 percent yield based on the halide used) of p-biphenylylethane-d_2 and 0.000728 g (3.32×10^{-6} mole, 0.056 percent recovery) of unreacted halide. A 0.299 g sample of this crude neutral material was sublimed at 65° and 50 microns pressure to give 0.0698 g of a mixture of solid and liquid. The nmr spectrum of this sublimate showed that it was predominantly some lubricant containing a small amount of an unknown compound. VPC of the acidic material (as methyl esters) showed that it contained 11 compounds in an overall yield of 0.164 g and ca. half of which was a compound of relative retention time 2.62 (based on methyl p-biphenylylpropanoate-d_2), and methyl 3-p-biphenylyl-propanoate-d_2 was obtained in less than 0.00613 g yield.

In run 5, a solution of 4.08 g (0.0307 g atom) of cesium in 250 ml of freshly distilled tetrahydrofuran was stirred at reflux for 30 minutes and then a solution of 2.89 g (0.0132 mole) of the halide in 25 ml of tetrahydrofuran was added dropwise over a period of 31 minutes. The first portion of halide added caused the appearance of a red color in the solution

and the final color was deep red. The resulting solution was stirred at reflux for five minutes, cooled at room temperature for 10 minutes, and then carbonated. The product was worked up in the usual manner to give 1.42 g (0.00772 mole) of a semi-solid neutral material and 1.65 g (0.00724 mole) of a light yellow semi-solid acidic material. VPC of the crude neutral material produced 0.470 g (0.00256 mole, 19.4 percent yield based on the halide used) of p-biphenylylethane-d_2 and 0.121 g (0.000720 mole, 5.5 percent yield, on the same basis) of a compound identified by comparison of VPC retention time as p-biphenylylmethane. A 1.35 g sample of this crude neutral material was sublimed twice at 70° at 70 microns pressure to give 0.488 g of pale yellow semi-solid, which was recrystallized from pentane to yield 0.210 g of white solid, m.p. 29-31° (premelting ~ 25°). The nmr spectrum [a multiplet centered at 2.74 τ (9.00 H), aromatic hydrogens; a doublet centered at 7.42 τ (1.01 H, J = 7.5 Hz), methylene group adjacent to the aromatic ring; and a singlet on top of a triplet centered at 8.81 τ (2.15 H), methyl group] indicated that it was a mixture of 47.9 percent of p-biphenylylethane-2,2-d_2 and 52.1 percent of p-biphenylylethane-1,1-d_2. VPC of the crude acidic material (as methyl esters) showed that it contained 0.193 g (0.000799 mole, 6.05 percent based on the halide used) of an ester of relative retention time 0.75 together with 0.0048 g (1.98×10^{-5} mole, 0.15 percent yield, on the same basis) of a compound at relative retention ca. 0.66. The above acidic product was converted into methyl esters and then sublimed three times at 80° at 50 microns pressure to give 0.151 g of a liquid. The nmr spectrum [a multiplet centered at 2.75 τ (9.00 H), aromatic hydrogens; a singlet at 6.41 τ (3.00 H), methoxyl group; a doublet (J = 7 Hz) centered at 6.21 τ (0.98 H); a doublet (J = 7 Hz)

centered at 8.48 τ (1.1 H) together with an absorption at 8.61 τ (0.63 H) apparently from an impurity] indicated that this was predominantly methyl 2-p-biphenylylpropanoate-3,3-d_2 contaminated by impurities possibly from lubricating oil.

Reaction of 1-Chloro-2-p-biphenylylethane with Potassium

Into the usual apparatus for alkali-metal reactions was placed 250 ml of freshly distilled tetrahydrofuran. To this solvent under a nitrogen atmosphere was added 0.478 g (0.0123 g atom) of potassium. The solution was heated with stirring at the boiling point for one hour. A solution of 1.20 g (0.00553 mole) of 1-chloro-2-p-biphenylylethane in 25 ml of dry THF was added dropwise at the boiling point of the solvent over a period of eight minutes and stirring and heating were maintained for another five minutes. The first portion of the halide added caused a red color to appear in the solution and the final color was dark reddish brown. After cooling at room temperature for 10 minutes, the contents of the flask were forced onto a large excess of crushed solid carbon dioxide. Ether extraction yielded 1.22 g of a semi-solid material. Acidification and extraction with ether gave 0.394 g of a semi-solid acidic product. A 1.19 g sample of the crude neutral material was sublimed at 100 microns pressure and a bath temperature of 60° to give 0.544 g of light yellowish oily sublimate. VPC of this sublimate showed only a single peak identified by comparison of retention time as p-biphenylylethane. A 0.387 g of this sample was sublimed the second time at 60° and 100 microns pressure to give 0.153 g of sublimate. The nmr of this sublimate [a multiplet centered at 2.87 τ (9.00 H), aromatic hydrogens; a quartet centered at 7.58 τ (1.98 H, J = 7.5

Hz), methylene group adjacent to the aromatic ring; and a complicated absorption at 8.8 to 9.2 τ with a total of 12.8 H which covers a triplet centered at 9.0 τ (J = 7.5 Hz) assigned to the methyl group] indicated that this sample was p-biphenylylethane contaminated by something resembling lubricating oil. (Possibly the oil originated from the ball bearing used or from the Nujol in which the potassium was stored.)

The above 0.394 g of semi-solid crude acidic product was reacted with diazomethane to give 0.392 g of crude esters, VPC of which showed that it contained 0.0646 g (0.000269 mole, 4.86 percent yield based on the halide used) of an ester with a relative retention time of 0.75 (based on methyl 3-p-biphenylpropanoate) and 0.00239 g of another ester having a relative retention time of 0.66. A 0.320 g of this crude ester product was sublimed at 85° and 200 microns pressure to give 0.0656 g of sublimate. The nmr spectrum [a multiplet centered at 2.75 τ (9.00 H), aromatic hydrogens; a quartet centered at 6.47 τ (1.1 H), methylene group adjacent to the aromatic ring; a singlet at 6.53 τ (3.0 H), methoxyl group; a doublet centered at 8.64 τ (ca. 3.5 H), methyl group which was contaminated by impurities possibly from the lubricant of the bearing or Nujol used to store the potassium] indicated that this ester was predominantly methyl 2-p-biphenylylpropanoate.

In the second run, potassium (0.455 g, 0.0116 g atom) was placed in 250 ml of freshly distilled THF and this mixture was stirred at the boiling point of THF for one hour. Then to this light orange solution at reflux was added dropwise a mixture of 0.847 g (0.00391 mole) of 1-chloro-2-p-biphenylylethane and 0.945 g (0.0127 mole) of freshly distilled t-BuOH over a period of five minutes. There was no appreciable color change.

The solution was stirred at reflux for an additional five minutes and then cooled at room temperature for 10 minutes before carbonation. A usual work-up yielded 1.14 g of wet, solid neutral material and 0.143 g of a pale yellow oily acidic product. A 1.08 g sample of the neutral material was sublimed three times at 65° and 100 microns pressure to give 0.550 g of solid material, m.p. 59-77° (with premelting and residue). VPC showed that this sublimate contained 35.0 percent of p-biphenylylethane, 62.3 percent p-biphenylylethene, and some 2.7 percent of a compound which had shorter retention time (relative retention time: 0.76 based on p-biphenylylethane as standard). A 0.373 g sample of this sublimate was recrystallized from ethanol to give 0.100 g, m.p. 103-112°. The nmr of this solid showed that it contained vinylbiphenyl as major component contaminated by 15 percent of p-biphenylylethane. No effort was made to identify the acidic material.

Reaction of 1-Chloro-2-p-biphenylylethane-1,1-d_2 with Potassium

To 250 ml of freshly distilled tetrahydrofuran was added 0.449 g (0.0115 g atom) of potassium. The solution was stirred with refluxing for 90 minutes and then a solution of 1.14 g (0.00520 mole) of 1-chloro-2-p-biphenylylethane-1,1-d_2 in 25 ml of tetrahydrofuran was added dropwise at the boiling point of the solvent over a period of five minutes. The first portion of halide added caused the appearance of a reddish brown color in the solution and the color after the completion of the addition was brown. Stirring was continued at reflux for an additional five minutes and then the solution was cooled at room temperature for 10 minutes before

carbonation. The product was worked up in the same manner as in the previous experiment yielding 0.340 g of a tarry acidic material and 1.16 g of semi-solid neutral material. A 1.10 g sample of this neutral material was sublimed at 90° and 150 microns pressure to give 0.564 g (61.2 percent based on the chloride used) of a semi-solid sublimate. A 0.410 g sample of this sublimate was further sublimed twice at 70° and 100 microns to give 0.256 g of a light yellow semi-solid. One recrystallization of this material from pentane gave 0.0410 g of a solid product, m.p. 31.5-32.5°. The nmr spectrum [a multiplet centered at 2.87 τ (9.00 H), aromatic hydrogens; a doublet centered at 7.52 τ (0.93 H), methylene group adjacent to the aromatic ring; and a singlet on top of a triplet at 8.94 τ (2.03 H), methyl group]* indicated that this neutral product contained 47.1 percent of p-biphenylylethane-2,2-d_2 and 52.9 percent of p-biphenylylethane-1,1-d_2.

A blank test, to demonstrate the thermal stability of 1-chloro-2-p-biphenylylethane-1,1-d_2 under the general reaction conditions, was conducted by adding dropwise over a period of 11 minutes a solution of 0.301 g of the chloride in 25 ml of tetrahydrofuran to 250 ml of refluxing tetrahydrofuran in the regular apparatus for alkali metal reactions. The resulting solution was stirred at reflux for five minutes and then allowed to stand at room temperature without stirring for two hours. After removing THF under partial vacuum, the residue was sublimed twice at 50° at 50 microns pressure to give 100 percent recovery of the chloride. The nmr of this sample showed no rearrangement within experimental error.

The acidic product was converted to the methyl esters by reacting

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*An external TMS standard was used.

with diazomethane. VPC showed that two esters of shorter retention times than that of methyl 3-p-biphenylylpropanoate were obtained in yields of 0.00710 g (relative retention time: 0.75 based on methyl 3-p-biphenylylpropanoate) and 0.000963 g (relative retention time 0.66). A 0.314 g sample of this crude ester was sublimed at 90° at 150 microns pressure to give 0.0637 g of oily sublimate which apparently, due to the presence of impurities, did not give a simple enough nmr spectrum for the identification of any single compound.

In run 2, a solution of 0.411 g (0.0105 g atom) of potassium in 250 ml of freshly distilled tetrahydrofuran was stirred at reflux for one hour. Stirring and heating were interrupted and the mixture was allowed to stand for 45 minutes until most of the metal floated on the surface of the solution. Then a solution of 0.616 g (0.00281 mole) of 1-chloro-2-p-biphenylylethane-1,1-d_2 and 1.59 g (0.0212 mole) of t-BuOD in 10 ml of tetrahydrofuran was added immediately. There was no evidence of vigorous reaction. Stirring and heating were resumed and the solution was stirred at reflux for five minutes before carbonation. A usual work-up yielded 0.860 g of neutral material. VPC analysis of this neutral product is given in Table 11. A 0.789 g sample was sublimed twice at 75° and 50 microns pressure to give 0.277 g of crystals, m.p. 100-111°, which was recrystallized from ethanol to give 0.115 g of white crystals, m.p. 116.5-118°. The nmr [a singlet on top of a multiplet at 2.69 τ (9.0 ± 0.3 H), aromatic hydrogens; a broad singlet at 3.42 τ (1.0 H), vinyl hydrogen adjacent to the aromatic ring] showed that it was pure p-$PhC_6H_4CH{=}CD_2$.

Table 11. Vapor-Phase Chromatographic Analysis of the Neutral Material in Run 2

Relative Retention Time	Peak Area (%)	Identification
0.42	0.77	Unknown
0.62	0.77	p-Biphenylylmethane
0.72	11.92	Unknown
0.80	1.15	Unknown
1.00	6.15	p-Biphenylylethane-d_2
1.12	79.23	p-Ph-$C_6H_4CH{=}CD_2$

VPC conditions: column, 6'$\frac{1}{8}$", 5% SE 30; column temperature 153°; flow rate, 26 mm; pressure, 60 psig.

In run 3, a solution of 0.750 g (0.0192 g atom) of potassium in 250 ml of freshly distilled tetrahydrofuran was stirred at reflux for one hour. To this solution at reflux was added dropwise a solution of 1.51 g (0.00689 mole) of the halide and 1.60 g (0.0213 mole) of t-BuOD in 25 ml of tetrahydrofuran over a period of 15 minutes. The resulting light yellow solution was stirred at reflux for an additional five minutes, allowed to stand at room temperature for five minutes, and then carbonated. Ether extraction gave 1.40 g of a light yellow semi-solid neutral material and the alkaline residue yielded 0.0483 g of an oily acidic material. VPC of the neutral product gave p-biphenylylethane (A), p-biphenylylethene (B), and a compound (C) with a relative retention time of 0.74 (based on p-biphenylylethane as standard) in relative yields of 39.1 percent, 52.9 percent, and 9.0 percent, respectively. A 1.39 g sample of this crude

product was sublimed at 53° at 10 microns pressure to give three fractions: (1) 0.343 g, m.p. 29-73°, VPC showed a ratio of ca. 1.0 : 0.9 : 0.3 of A : B : C; (2) 0.257 g in 1.0 : 2.2 ratio of A : B (no C); (3) 0.247 g in 1.0 : 2.8 : 0.2 ratio of A : B : C. A 0.321 g sample of (1) above was recrystallized from pentane to give (1a) 0.0520 g, m.p. 94-106°, VPC (mole percent) showed 26.5 percent A and 73.5 percent B; (1b) 0.0522 g, m.p. 91-104°, 35.5 percent A and 64.5 percent B; (1c) 0.0376 g, m.p. 65-92°, 51.6 percent A and 48.4 percent B. This last sample (1c) was analyzed by nmr and found to contain 9.00 H centered at 2.86 τ (m, aromatic hydrogens), 0.49 H at 3.45 τ (s, olefinic hydrogens alpha to the aromatic ring), 0.71 H centered at 7.52 τ (s on top of a t, methylene group alpha to the aromatic ring), 0.14 H centered at 8.9 τ (t, J = 7 Hz, methyl group); this spectrum corresponds to a mixture of 49 percent p-biphenylylethene-2,2-d_2 (with p-biphenylylethene-1-d_1 constituting none or less than 10 percent of the olefinic portion), 51 percent p-biphenylylethane containing 1.4 ± 0.1 alpha and 0.28 ± 0.02 beta hydrogens. The same sample was also analyzed by mass spectrometer and found to have, for B, mainly d_2 contaminated by less than 3.2 percent d_1 compound; for A, 15.9 percent d_2, 49.8 percent d_3, 29.1 percent d_4, 4.2 percent d_5, and 1.0 percent d_6 compounds. Further discussion of these products is presented in the next chapter.

CHAPTER V

DISCUSSION

Syntheses

1-Chloro-2-*p*-biphenylylethane

This chloride was prepared in an overall yield of about 30 percent from 4-acetylbiphenyl according to the synthetic route shown in Figure 1. The intermediate *p*-biphenylylacetic acid was prepared in 63 percent yield from the starting material, 4-acetylbiphenyl. The solvent most commonly used for the reduction of organic acids with lithium aluminum hydride is diethyl ether. Because of the low solubility of *p*-$PhC_6H_4CH_2CO_2H$ in this solvent, tetrahydrofuran was used instead. When a limited quantity (*ca.* 1:1 ratio) of the reducing agent was used, a poor yield of the desired carbinol, 2-*p*-biphenylylethanol, was obtained, and good yields of some higher melting compound, apparently a product of an intermediate reduction stage together with the starting acid were recovered. Only when a large excess of the reducing agent (3:1 molar ratio) was used was there obtained an almost quantitative yield of the desired carbinol. The necessity of using large excess reducing agent was conceivably due to the poor quality of commercial lithium aluminum hydride employed in this reduction. Attempts to convert this carbinol into the corresponding chloride with thionyl chloride in both triethylamine and tri-*n*-butylamine resulted in the formation of 3-10 percent of sulfite ester and some 15 percent of unreacted carbinol among other materials. The desired chloride was successfully prepared

in over 60 percent yield by reacting the carbinol with thionyl chloride in pyridine.

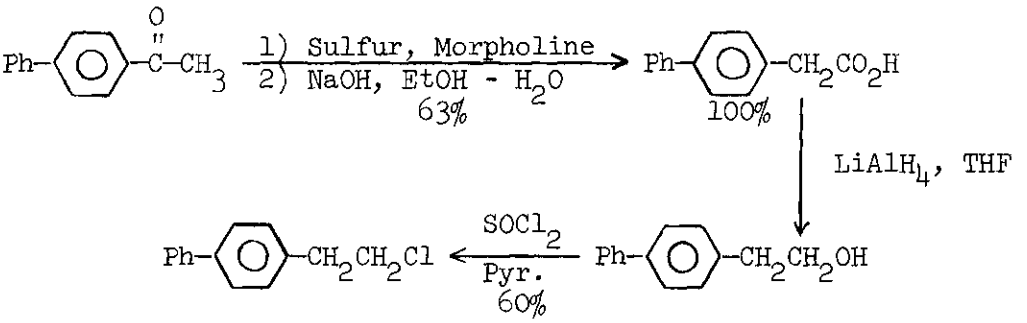


Figure 1. Synthetic Route to 1-Chloro-2-p-biphenylylethane

1-Chloro-2-p-biphenylylethane-1,1-d_2

In view of the difficulty encountered in the reduction of p-biphenylylacetic acid with lithium aluminum hydride, the synthetic process of the title compound was slightly modified to follow the synthetic route shown in Figure 2. p-Biphenylylacetic acid was first converted in good yield (> 90 percent) into the methyl ester by a standard method. The reduction of methyl p-biphenylylacetate with a good grade of lithium aluminum deuteride (ca. 1.2:1 ratio of reducing agent to ester) in tetrahydrofuran gave over 90 percent yield of the desired carbinol. The conversion of this carbinol, 2-(p-biphenylyl)ethanol-1,1-d_2, into the desired chloride was carried out according to the method used for the protium compound. The overall yield from p-biphenylylacetic acid was 62 percent.

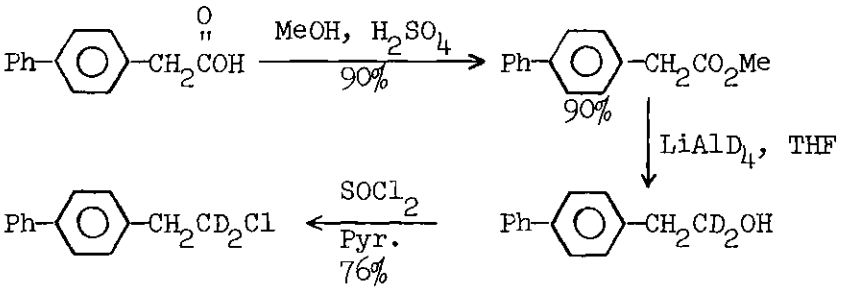
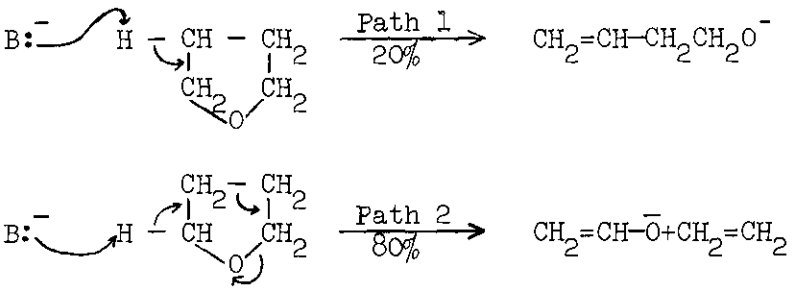


Figure 2. Synthetic Route to 1-Chloro-2-p-biphenylylethane-1,1-d_2

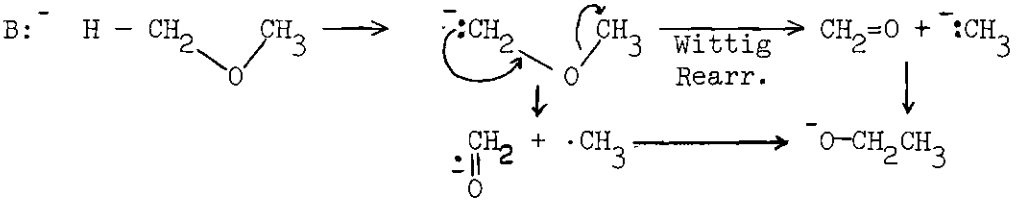
Syntheses of Simple Primary Carbanions

The synthesis of butyl anion (summarized in Table 3) from the reaction of 1-chlorobutane with Cs-K alloy at -40° and with Cs-K-Na alloy at -70° in tetrahydrofuran gave, after carbonation, valeric acid in yields ranging from 0.43 to 5.4 percent after times of two to six minutes. The same synthesis in diethyl ether yielded the desired carbanion in ca. 5 percent at -36° with the binary alloy and at -95° with the ternary alloy; however, the reaction of this ternary alloy at -70° gave 19 percent butyl anion in diethyl ether after 20 minutes. Primary alkyl potassium compounds are known to abstract protons even from a hydrocarbon solvent.[5] Szwarc and co-workers[37] have shown that diphenylacetylene dianion cleaves tetrahydrofuran 20 percent by path 1 and 80 percent by path 2.

(37) G. Levin, J. Jagur-Grodzinski, and M. Szwarc, J. Am. Chem. Soc., 92, 2268 (1970).



Diethyl ether can undergo a similar cleavage by a carbanion as shown in path 1 above, while dimethyl ether can likely undergo the following cleavage:



Diethyl ether could probably be cleaved by a carbanion in a similar fashion. In the present work, the reaction of 1-chlorobutane with the same ternary alloy in dimethyl ether at temperatures ranging from -60 to -107° gave from 0.2 to 13.3 percent yields of butyl anion. The extremely low temperature (-107°) did not seem to favor the yield of the desired carbanion but butyl anion seemed to be fairly stable at this temperature. Dimethyl ether did not prove to be better than diethyl ether as a medium for the synthesis of primary alkyl carbanions. Cesium alloys gave a bluish color in tetrahydrofuran and in dimethyl ether but not in diethyl ether. The lower yields of butyl anion in tetrahydrofuran than in diethyl ether may possible be due to the greater solubility hence greater reactivity of this carbanion in tetrahydrofuran.

Since a carbanion can also couple with the unreacted halide to yield a Wurtz dimer or serve as a base to dehydrohalogenate the halide,[2]

$$RM + RX \longrightarrow R - R + MX$$

$$RM + R'CH_2CH_2X \longrightarrow RH + R'CH = CH_2 + MX$$

an alternative synthesis which can cut down these undesired side reactions should prove to be preferable. Hence, di-n-butylmercury was chosen to react with the same ternary alkali metal alloy.[5,38,39]

The cleavage of di-n-butylmercury with Cs-K-Na alloy in tetrahydrofuran at -70° for a total of 14 minutes gave butyl anion in 34 percent yield. A prolonged reaction to 74 minutes resulted in a tremendous decrease in yield of the desired carbanion to only 0.5 percent. The same cleavage reaction in diethyl ether at -70° for 15 minutes produced 37 percent of the desired carbanion together with 44 percent of unreacted di-n-butylmercury. When the reaction was run for 30 minutes longer, the yield of butyl anion decreased to 11 percent with almost complete reaction of di-n-butylmercury (only 2.2 percent unreacted). An attempt to run an nmr spectrum of the carbanion prepared from the cleavage of di-n-butylmercury in diethyl ether was unsuccessful, apparently because either the half life (ca. eight minutes in diethyl ether) of butyl anion is too short or this carbanion is not sufficiently soluble in diethyl ether or both. The same reaction in dimethyl ether at -70° for 15 and 45 minutes gave only 0.2 per-

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(38) R. A. Finnegan, Tetrahedron Letters, 851 (1963).

(39) R. A. Finnegan, Trans. N.Y. Acad. Sci., 27, 730 (1965).

cent yield of butyl anion. Thus the cleavage of dialkylmercury is superior to that of alkyl halides for the syntheses of primary alkyl anions, and butyl anion is short-lived and probably not very soluble in the ethereal solvents used.

Because of the difficulty in the analysis of neutral products from the cleavage of both 1-chlorobutane and di-n-butylmercury, a higher boiling halide likely to give neutral products suitable for analyses was chosen. The reaction of 1-chloroheptane with ternary cesium alloy in tetrahydrofuran at -65° for 10 minutes gave absolute yields of 1.5 percent heptyl anion, 24 percent heptane, 14 percent 1-heptene, 12 percent tetradecane, and 29 percent unreacted chloride. A prolonged reaction time of 26 minutes resulted in a decrease in yield of the desired carbanion to 0.9 percent, a slight increase (to 26 percent) of heptane, and unchanged yields of the other two products.

In order to test the solvent effect on the stability of alkyl carbanions, trimethylamine was considered as an alternative to ethereal solvents because the protons of this amine are expected to be less acidic than those of ethereal solvents. The reaction of 1-chloroheptane with ternary cesium alloy in trimethyl amine at -45° for 14 minutes yielded 5.0 percent of heptyl anion, 9.2 percent of heptane, 2.5 percent of 1-heptene, 6.1 percent of tetradecane, and 1.4 percent of unreacted chloride. When the reaction was run for another 20 minutes, the yield of the desired anion increased to 7.5 percent, and the yields of heptane, 1-heptene, and tetradecane decreased to 1.8 percent, 0.5 percent, and 5.0 percent, respectively. The decreases in yields of hydrocarbons could be accounted for by the fact that they might have been further metalated either by carbanions already

formed or by the metals themselves. Since the material balances were rather poor, a better explanation seems needed. Because of the high vapor pressure of trimethylamine at room temperature, the deficiency in the neutral products could best be explained by the solvent distillation of these compounds when the carbonation products were allowed to stand at room temperature overnight.

Rearrangement During Synthesis of Neophyllithium

It is of interest to know whether neophyllithium (I), $PhCMe_2CH_2Li$, undergoes rearrangement to give 1,1-dimethyl-2-phenylethyllithium (II), $PhCH_2CMe_2Li$; therefore, the reaction of neophyl chloride with lithium was studied. In tetrahydrofuran at -60° for 35 minutes this reaction gave a bright yellow solution of lithium reagent. Carbonation produced 72 percent yield of carboxylic acids which, according to VPC of the methyl esters, contained relative yields of 93.6 percent 3-methyl-3-phenylbutanoic acid (III) and 6.4 percent 2,2-dimethyl-3-phenylpropanoic acid (IV). Acid (III) corresponds to neophyllithium and acid (IV) was the product due to a phenyl group migration. When the solution of neophyllithium prepared at -60° was stirred at -70° for four hours followed by carbonation, the yields of the carboxylic acids changed only slightly (to 71 percent) and the proportion of acid (IV) decreased to 5.5 percent. Another four hours of reaction at -70° lowered the proportion of (IV) to 3.9 percent.

Another reaction run at -65° for two hours gave, upon carbonation of a small portion, 81 percent of acids which consisted of 94 percent acid (III) and 6 percent acid (IV). When the solution of the neophyllithium was warmed up to -50° and then to -40° for a total of two and one-half hours, the yields of carboxylic acids decreased slightly to 75 percent.

The proportion of (IV) decreased from 6.0 percent at -65° to 5.2 percent at -50° and then to 3.5 percent at -40°.

Neophyllithium has previously been found to undergo decomposition at both 0° and 30°.[20] This decomposition was proposed to be due to the protonation of the organolithium compounds by the solvent. A solution of neophyllithium was prepared at -65° in the usual manner and allowed to warm to 4° and stand at that temperature without stirring for four hours before carbonation. The yield of carboxylic acids in this reaction decreased from 75 percent during preparation at -65° to 7.8 percent at 4° for four hours. VPC of the acidic products (as methyl esters) formed at -65° gave relative yields of 92.5 percent acid (III) and 5.6 percent acid (IV), while the same analysis of the acids formed at 4° using column V showed three peaks in relative yields (relative retention time) of 30.0 percent (0.85), 38.3 percent (1.00), and 29.9 percent (1.25), and both methyl esters of acid (III) and o-t-butylbenzoic acid had the same relative retention time of 1.00. Analysis of the latter using column IV gave relative yields (relative retention time) of 50.4 percent (0.86), 18.7 percent (1.00), and 29.2 percent (1.37); under these conditions the methyl esters of o-t-butylbenzoic acid and acid (III) have relative retention times of 0.86 and 1.00, respectively. These analyses indicated that acid (III) and o-t-butylbenzoic acid were obtained in relative yields of 18.7 percent and 19.6 percent, respectively, with the remainder approximately equal amounts of two unidentified compounds.

Williams has reported that the same reaction at 0° for one hour gave 25 percent of an acidic product consisting of 98 percent acid (III) and 2 percent of ortho-t-butylbenzoic acid. Thus, apparently a prolonged

reaction has resulted in the formation of undesired unknown products. The neutral material was also analyzed by VPC and found to give absolute yields of 77 percent t-butylbenzene, 7.9 percent i-butylbenzene, and 2.9 percent of unreacted chloride. Thus i-butylbenzene seems to arise by protonation of 1,1-dimethyl-2-phenyllithium (II) and t-butylbenzene similarly from 2-methyl-2-phenylpropyllithium (I); the chief source of such protons appears to be the solvent tetrahydrofuran. The cathodic reduction of neophyl chloride at a mercury cathode in aqueous N,N-dimethylformamide has been reported to give these two hydrocarbons with a composition of 93.6 percent t-butyl- and 6.4 percent i-butylbenzene.[40]

Attempts were made to increase the extent of rearrangement of neophyllithium by using a chelating agent, N,N,N',N'-tetramethylethylenediamine (TMEDA), which has been reported to activate some organolithium compounds. A solution of neophyllithium prepared at -65° in tetrahydrofuran was mixed with an equivalent of TMEDA and the mixture was stirred at -65° to -30° for two hours and finally at -30° for an additional two hours before carbonation. The resulting acidic product (77 percent yield) consisted of 97.8 percent of acid (III) and 2.2 percent of acid (IV). Thus the addition of a limited quantity of the chelating agent has not promoted rearrangement. When the reaction was repeated using a larger excess (ca. 16 TMEDA:1 RLi) of the diamine at -20° for three hours followed by carbonation, the acidic product was obtained in 52 percent yield. Compound (III), which was obtained in 34 percent absolute yield, was the only volatile acidic product present in significant amount. There was no evidence of the survival of

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(40) L. Eberson, Acta Chem. Scand., 22, 3045 (1968).

compound (II) under these conditions. The neutral product was found to contain absolute yields of 26 percent of t-butylbenzene and 5.5 percent of i-butylbenezene. Thus the addition of excess TMEDA and the increase in reaction temperature have not increased the extent of rearrangement, but on the contrary, possibly have accelerated the protonation of both organolithium compounds (I) and (II).

From the energies of activation for 1,2-rearrangements calculated by Orchin and his co-workers, one would estimate that a free radical rearrangement (E_{act} 7.84 ev) would be more favorable than an anionic rearrangement (E_{act} 9.46 ev) for phenyl group.[19] Organolithium compounds have been reported to form radical-anions photochemically. However, several attempts to accelerate the rearrangement of neophyllithium photochemically were unsuccessful. In a typical run, neophyllithium was prepared in 86 percent yield at -65° in tetrahydrofuran and the excess lithium was removed by filtration. The organolithium solution was then divided into two portions; one portion was irradiated with a 450 watt Hanovia lamp at -74° for 13½ hours and then carbonated, and the other portion was allowed to stand under the same conditions without the uv light for the same length of time before carbonation. The photochemical reaction produced acidic and neutral material in a ratio of 1.10 : 1.00; the thermal decomposition reaction gave acidic and neutral material in a ratio of 0.898 : 1.00. The acidic products were analyzed as methyl esters by VPC and found to contain 97 percent of (III) and 3 percent of (IV) in the photochemical reaction; and 96.5 percent of (III) and 3.5 percent of (IV) in the thermal decomposition reaction. Thus the composition of the acidic product from the photochemical reaction was essentially identical with that of the thermal decomposition. In three

other attempts using either a 200 watt Hanovia lamp at -70° for two hours or a 450 watt Hanovia lamp at -70 ± 5° for 12 hours, there was obtained some 38 to 50 percent yields of acidic products. These acidic products were analyzed as methyl esters by VPC and found to consist of 98 ± 1 percent of (III) and 1 ± 1 percent of (IV).

Since the rearrangement products (IV) and i-butylbenzene were always observed in small amounts (ca. a total of 6 percent), it was conceivable that these rearranged products were originated from one of the four possible sources: (1) contamination of the starting neophyl chloride by a minor imputiry, i.e., 2-chloro-2-methyl-1-phenylpropane, (2) rearrangement of the former under reaction conditions to give the latter before the reaction of lithium metal, (3) thermal rearrangement to (II) and i-butylbenzene during the initiation, and (4) rearrangement promoted by the methyl iodide used in initiating the reaction. According to VPC analysis, the starting neophyl chloride was free from isomeric impurities; in particular it was demonstrated that the chloride related to (II), i.e., 2-chloro-2-methyl-1-phenylpropane, was present (if at all) in an amount of less than 0.5 percent. Moreover, reduction of the starting chloride with sodium in refluxing dioxane-t-pentyl alcohol gave t-butylbenzene containing less than 1.2 percent of i-butylbenzene. It is, therefore, very unlikely that the rearrangement products could arise from impurities in the starting halide. The possibility that neophyl chloride could have been isomerized under the reaction conditions to 2-chloro-2-methyl-1-phenylpropane was disproved by a blank experiment. Thus a solution of neophyllithium prepared in tetrahydrofuran at -65° was reacted at this same temperature with an equivalent of neophyl chloride for five hours and the resulting solution was carbonated.

The chloride which was recovered in 85 percent yield was found to be neophyl chloride without any contamination by isomeric halides. Thus, the first and second possibilities above were disproved. The third possibility was disproved by a preparation run at -10° for one hour, which gave absolute yields of 0.9 percent of rearranged acid (IV), 5.8 percent of i-butylbenzene, and mostly unrearranged acid (III). The fourth possibility above was also disproved by experiments in which the methyl iodide was omitted without changing the results (save for somewhat more unreacted neophyl chloride than usual in the products).

Therefore, it is concluded that neophyl chloride reacts with lithium metal by a one-electron transfer process to give neophyl radical which in part is free enough from metal to undergo the known 1,2-migration of phenyl; reduction of the radicals with lithium then gives the organolithium products (I) and (II).[41] A similar explanation has been advanced to account for the rearranged hydrocarbons formed during reaction of neophyl chloride with magnesium,[18a] the cathodic reduction of neophyl chloride,[40] and for racemization (but no rearrangement of phenyl) during reaction of optically active 1-halogen-1-methyl-2,2-diphenylcyclopropane with magnesium and lithium.[42]

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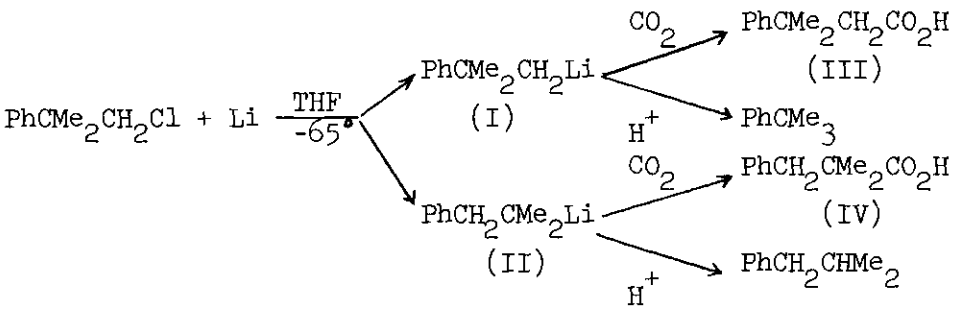
(41) E. Grovenstein, Jr. and Yao-Ming Cheng, Chem. Comm., 1970, 101.

(42) H. M. Walborsky and A. E. Young, J. Am. Chem. Soc., 86, 3288 (1964); H. M. Walborsky and M. W. Aroneff, J. Organometal. Chem., 4, 413, (1965).



The metal-halogen interchange reactions of alkyllithium compounds and alkyl halides have been reported to take place by a two-step one-electron transfer process.[43] One attempt was made to promote free radical rearrangement of neophyllithium by the addition of iodine. Neophyllithium was prepared at -65° in tetrahydrofuran and then reacted with approximately one-half equivalent of iodine at -65° for a total of 64 minutes before carbonation. The carbonated product yielded 10 percent of carboxylic acid, which consisted of 98 percent of acid (III) and 2 percent of acid (IV). In this reaction, t-butylbenzene and i-butylbenzene were obtained in absolute yields of 9.8 percent and 2.3 percent, respectively. Most of the organolithium compounds originally generated were apparently lost by the formation of Wurtz coupling products. The original thought was that the addition of iodine would generate some alkyl iodide which might undergo metal-halogen interchange with the remaining neophyllithium to produce neophyl radicals; neophyl radicals in turn would undergo rearrangement to give rearranged products of normal molecular weights. This experiment has failed to give the expected results. Another attempt was made in the hope

(43) H. R. Ward, R. G. Lawler, and R. A. Cooper, J. Am. Chem. Soc., 91, 746 (1969); A. R. Lepley and R. L. Landau, ibid., 91, 749 (1969).

that the addition of an alkyl halide itself might accelerate the rearrangement of neophyllithium. In an experiment, neophyllithium was prepared at -65° in tetrahydrofuran and then warmed to -10° for one hour to destroy most of the rearranged organolithium compound (II). The temperature was again lowered to -65° and the solution was divided into two parts; to one of these was added approximately one-half equivalent of ethyl iodide and to the other half was added approximately the same molar ratio of neophyl chloride. The portion to which ethyl iodide had been added was allowed to stand at -60° for up to 15 minutes and then carbonated. This reaction resulted in a tremendous decrease in yield (to 3.1 percent) of acid (III); two neutral products which have retention times between those of butylbenzene and neophyl chloride were observed in significant amount. These two compounds (obtained in 23 percent and 3 percent absolute yields) were possibly coupling products of ethyl iodide with organolithium compounds (I) and (II). The portion to which neophyl chloride had been added was allowed to stand at -65° for up to one hour. This reaction did not affect the yields of carboxylic acids significantly. Both ethyl iodide and neophyl chloride did not alter the yields of t-butylbenzene and i-butylbenzene (identity confirmed by nmr)* noticeably. The yields of these two hydro-

*The nmr spectrum of t-butylbenzene showed a multiplet centered at 2.83 τ (5 H), a singlet at 8.78 τ (9 H); while that of i-butylbenzene showed a multiplet centered at 2.92 τ (5 H), a soublet centered at 7.58 τ (2 H, J = 7 Hz), a multiplet centered at 8.25 τ (1 H, J = 6.5 Hz), a doublet centered at 9.13 τ (6 H, J = 7 Hz); that of s-butylbenzene showed a multiplet at 2.88 τ (5 H), a sextet centered at 7.49 τ (1 H, J = 7 Hz), a quintet centered at 8.47 τ (2 H, J = 7 Hz), a doublet centered at 8.83 τ (3H, J = 7 Hz), and a triplet centered at 9.21 τ (3 H, J = 7 Hz).

carbons seemed to remain constant (19 percent for the former and 9 percent for the latter). Thus the addition of both iodine and alkyl halides has not accelerated the rearrangement of neophyllithium as indicated by the present (but incomplete) product analyses.

Two attempts were made to effect the rearrangement of neophyllithium by reacting it with a more reactive metal. Neophyllithium prepared at -65° in tetrahydrofuran was reacted with approximately three equivalents of Cs-K-Na alloy for one hour and then carbonated. The resulting acids gave relative yields of 80 percent acid (III), 5.5 percent acid (IV), and 14.5 percent of four unidentified acids. The neutral material produced absolute yields of 10.9 percent t-butylbenzene and 1.8 percent of i-butylbenzene. The same cleavage reaction was run at -10° for 45 minutes before carbonation. The acidic product consisted of 93 percent acid (III), 2.1 percent acid (IV), and 4.9 percent of three unidentified acids. The t-butylbenzene and i-butylbenzene were obtained in 21.2 percent and 4.78 percent absolute yields, respectively.

Reaction of Neophyl Chloride with Potassium and Potassium-Cesium Alloys

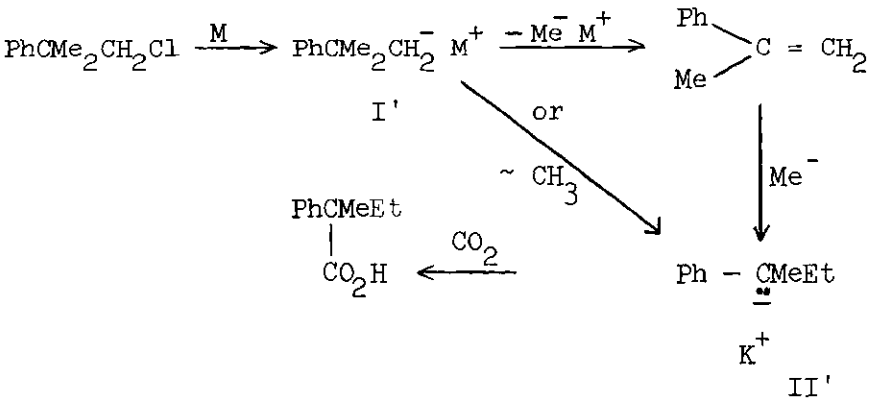
The reaction of neophyl chloride with potassium in refluxing tetrahydrofuran produced a reddish brown solution which, upon carbonation, gave some 6.7 percent absolute yield of oily acidic product and some 71 percent of volatile hydrocarbons, and the remainder nonvolatile neutral compounds. The acidic product was converted into methyl esters which were analyzed by VPC; this product was found to contain three major acids in an overall absolute yield of 0.58 percent, and none of these was identified as (III), (IV),

2-phenyl-2-methylbutanoic acid, or o-, m-, or p-t-butylbenzoic acid. The neutral product gave absolute yields of 64 percent t-butylbenzene, 6.2 percent i-butylbenzene (identity confirmed by nmr), and 0.1 percent unreacted neophyl chloride. Thus, under the reaction conditions, the organopotassium compounds initially formed during the reaction of neophyl chloride with potassium apparently were protonated by the solvent. The small amount of acidic products could possibly result from metalation of β,β-dimethylstyrene since reaction of neophyl chloride with a deficient quantity of sodium has previously been reported to yield t-tubylbenzene (34.6 percent), 1-methyl-1-phenylcyclopropane (11.9 percent), and β,β-dimethylstyrene (13.7 percent) along with unreacted neophyl chloride.[44]

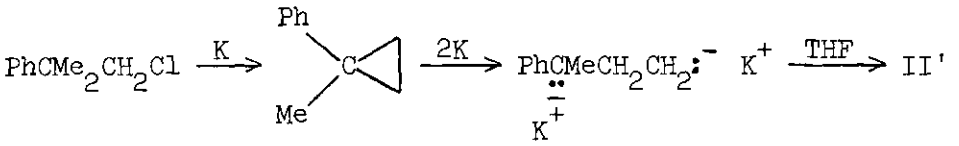
Neophyl chloride was also reacted with both a binary Cs-K alloy and a ternary Cs-K-Na alloy at lower temperatures to see whether there was any rearrangement. The reaction was studied with binary Cs-K alloy in tetrahydrofuran at -40° and -60° and gave 43 percent and 42 percent, respectively, of acidic mixtures. These acidic mixtures each contained at least seven compounds and among these 2-phenyl-2-methylbutanoic acid constituted from 7 to 10 percent (relative yields) of the volatile acidic mixture (or in absolute yield of 1.38 and 2.84 percent based on the chloride used). Two acids which constituted 0.5 to 1.8 percent of the volatile acid mixture could be a mixture of acid (III) and o-t-butylbenzoic acid, but they were not positively identified. The neutral products were found to give, in the run at -40°, absolute yields of 38 percent t-butylbenzene and 4.2 percent i-butylbenzene and/or s-butylbenzene. The reactions of neophyl chloride

(44) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., J. Am. Chem. Soc., 65, 1469 (1943).

with Cs-K-Na alloy were carried out in tetrahydrofuran at -63 ± 4° for two time intervals of 13 and 37 minutes. The 13 minutes reaction gave 42 percent of acidic product which contained at least seven volatile compounds, with 2-phenyl-2-methylbutanoic acid constituting 4.1 percent (1.1 percent absolute yield) of these. The corresponding neutral material produced absolute yields of 38 percent t-butylbenzene, 2.0 percent i-butylbenzene and/or s-butylbenzene, and 2.2 percent of unreacted neophyl chloride. The 37 minutes reaction gave 77 percent of acidic product which, according to VPC of the methyl esters, consisted of 9.0 percent (relative yield) of 2-phenyl-2-methylbutanoic acid (or ca. 4 percent absolute yield) with the remainder five unidentified acids. The neutral material from this run gave > 90 percent relative yield of t-butylbenzene. The 2-phenyl-2-methylbutanoic acid must arise from carbanion II'; this anion might be formed by a 1,2-migration of methyl in I' or via an elimination readdition mechanism:



Because of resonance stabilization, carbanion II' is expected to be more stable than carbanion I'. The following mechanism, however, cannot be completely ruled out:



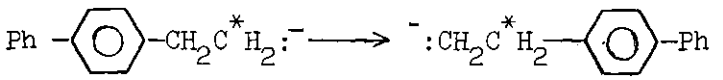
As quoted above,[44] both β,β-dimethylstyrene and 1-methyl-1-phenylcyclopropane have been obtained in the reaction of sodium with neophyl chloride.

Contrary to the reaction in tetrahydrofuran, the reaction of neophyl chloride with the same ternary cesium alloy in diethyl ether at -70° produced only 4.7 percent of acidic material; here 3-phenyl-3-methylbutanoic acid was formed in 0.86 percent yield and 2-phenyl-2-methylbutanoic acid in 0.018 percent yield (absolute).

In summary, the reaction of neophyl chloride with cesium alloys in tetrahydrofuran at -40° to -70° gives complex acidic products containing some product corresponding to methyl group migration of the original neophyl anion. The only reaction in which neophyl anion was observed was in diethyl ether apparently due to the low solubility of this primary carbanion in this solvent.

Analysis of p-Biphenylylethyl and p-Biphenylylethyl-d_2 Compounds by NMR Spectroscopy

In order to determine whether or not a p-biphenylyl group has undergone a 1,2-rearrangement across an ethyl system, it is essential that a suitable label be present to reveal such a migration and an analytical method available to monitor the process,



Early in the present work it was decided that deuterium would provide a useful label since the course of the rearrangement could be followed conveniently by nmr spectroscopy. In Table 12 are listed the nmr spectra of the compounds utilized in the present work. Spectral assignments can be made here with confidence because of the availability of the deuterium-labeled compounds of known structure. Also, the absence of absorptions in the deuterium compounds confirms their isotopic purity. The widely varying chemical shifts of the methyl and methylene protons in p-biphenylylethane make analysis for p-biphenylyl migration especially easy in this compound.

Syntheses and Stability of 2-Arylethyllithium

The synthesis of 2-phenethyllithium* (2-phenylethyllithium by the reaction of 1-chloro-2-phenylethane with lithium in tetrahydrofuran was, under the conditions used, reasonably successful. The reaction was initiated at 0° in the presence of methyl iodide and then conducted at -65° for two hours. Carbonation yielded 69 percent of 3-phenylpropanoic acid. The corresponding hydrocarbon, ethylbenzene, was obtained in 24 percent yield.

In general, the synthesis of an organoalkali compound of the structure $ArCH_2CH_2M$ from the corresponding halide would encounter a number of difficulties due to the tendency for dehydrohalogenation of the halide and

$$ArCH_2CH_2X \xrightarrow{B:^-} ArCH{=}CH_2 + HB + X^-$$

$$ArCH{=}CH_2 \xrightarrow{RM} \underset{M}{ArCH{-}CH_2R} \xrightarrow{ArCH=CH_2} \text{etc.}$$

*This lithium compound has been reported in literature (see U. S. Patent, 3069407, 1962) but no details were given for its synthesis.

Table 12. The nmr Spectra of p-Biphenylylethyl Compounds*

Compound	τ	Intensity	Multiplicity	Assignment
p-$C_{12}H_9CH_2CH_3$[a]	2.83	9.00	m	aromatic
	7.49	1.89	t	α-methylene
	8.87	3.04	q	methyl
p-$C_{12}H_9CH_2CD_2H$[a]	2.83	9.00	m	aromatic
	7.52	1.86	d	α-methylene
	8.93	1.16	t	methyl
p-$C_{12}H_9CH_2CH_2OH$	2.62	9.26	m	aromatic
	6.14	2.00	t	β-methylene[c]
	7.13	2.00	t	α-methylene[b]
	8.45[d]	1.16	s	OH
p-$C_{12}H_9CH_2CD_2OH$	2.62	9.3	m	aromatic
	7.19	2.0	s	α-methylene[b]
	7.75[d]	1.0	s	OH
p-$C_{12}H_9CH_2CH_2Cl$	2.88	9.39	m	aromatic
	6.44	2.00	t	β-methylene[c]
	7.06	2.00	t	α-methylene[b]
p-$C_{12}H_9CH_2CD_2Cl$	2.72	9.00	m	aromatic
	7.02	2.00	s	α-methylene[b]
p-$C_{12}H_9CH_2CH_2CO_2CH_3$	2.79	8.87	m	aromatic
	6.47	3.00	s	methoxyl
	7.20	2.12	Unsym. t	α-methylene[b]
	7.44	2.12	Unsym. t	β-methylene[c]
p-$C_{12}H_9CH_2CD_2CO_2CH_3$	2.70	9.00	m	aromatic
	6.41	3.01	s	methoxyl
	7.10	2.01	s	α-methylene[b]

*Carbon tetrachloride was used as solvent except in the case of the two alcohols where deuterochloroform was used as solvent.

[a]External TMS was used as standard.

[b]Methylene group adjacent to the aromatic ring.

[c]The other methylene group.

[d]The chemical shift of OH proton varies with concentration of solution.

for the olefin formed, $ArCh=CH_2$, to be polymerized by RM to give complicated products.

Most of the known carbanion rearrangements involving a 1,2-aryl migration have been limited to those which do not have any β-hydrogens.[15-17,45] The only examples which have been studied involving two β-hydrogens were found in the work by Cram and Dalton.[21] The reduction of 1,1-dideuterio-2-(1-naphthyl)-ethyl methanesulfonate and 1,1-dideuterio-1-methoxy-2-(1-naphthyl)-ethane with potassium in dimethoxyethane was found to give no rearrangement. In the same paper, the reactions of potassium with threo-2-phenyl-2-pentyl methanesulfonate in dimethoxyethane and of sodium with threo-3-phenyl-2-pentyl methanesulfonate in liquid ammonia were reported to give 6 and 3 percent of rearrangement, respectively.

The success in the synthesis of phenethyllithium raised the possibility of studying the syntheses and rearrangements of organoalkali compounds with two β-hydrogens. The starting compounds chosen for this study were 1-chloro-2-p-biphenylylethane and 1-chloro-2-p-biphenylylethane-1,1-d_2. The synthesis of 2-p-biphenylylethyllithium from the corresponding chloride and lithium metal is summarized in Table 13. The optimum conditions for this synthesis in tetrahydrofuran were found to be reaction of the halide with a large excess lithium (1 RCl: 16 Li) at -73° for a short period of time (20 minutes addition and 10 minutes subsequent stirring)(run 4). This reaction upon carbonation yielded 52 percent of 3-p-biphenylylpropanoic acid. During the reaction a pink color first appeared in the solution and

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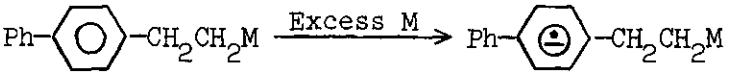
(45) H. E. Zimmerman and F. J. Smentowski, J. Am. Chem. Soc., 79, 5455 (1957).

Table 13. Reaction of 1-Chloro-2-p-biphenylylethane with Lithium

Run No.		1	2		3		4	5		6
RCl	g (mole)	4.68 (0.0216)	4.89 (0.0226)		4.98 (0.0230)		5.01 (0.0231)	5.01 (0.0231)		5.01 (0.0231)
Lithium	g (g atom)	0.591 (0.0851)	1.24 (0.179)		0.374 (0.0539)		2.55 (0.367)	2.50 (0.360)		2.55 (0.367)
Reaction Temp.		-70°	-70°		-70°		-74°	-73°		-75°
Time of Addition	min	32	20		30		20	14		22
Time of Stirring at Rxn. Temp.	min	293	38	118	110	140	10	6		28
Time of Standing after Filtration	min	none	none		none		none	65	240	60
Temp. of Standing								-65°	-65°	0°
Yield of Crude Acid	g (%)	1.05 (21.4)	0.851 (50.3)	1.42 (41.9)	0.0867 (3.62)	0.0850 (3.65)	2.73 (52.2)	0.629 (26.5)	0.483 (20.4)	1.97 (37.7)
m.p. of Crude Acid		94-121°	146-51°	128-46°	semi-solid		146-51°	148-51°	148-51°	145-50°
Yield of Volatile Acid	g (%)	0.332 (6.80)	0.689 (33.7)	0.840 (27.5)	0.0361 (1.53)	0.0599 (2.56)				
m.p. of Acid after Vacuum Sublimation		138-148°	150-2°	147-50°			150-1.5°			
Yield of Crude Neutral Products	g (%)	2.98 (75.7)	1.48	1.21 (44.0)	2.21	2.15	3.08	1.38 (72.2)	0.76 (68.2)	2.86 (67.9)

this gradually deepened into a brownish-red. At the end of the reaction a green color began to appear; this color is apparently due to formation of the radical anion of the biphenyl group (biphenyl radical anion is reported to be blue[46] in tetrahydrofuran). The yield of 2-p-biphenylylethyllithium decreased with decreasing relative amount of lithium metal used. When the preparation was carried out in the same solvent at -70° using only 15 percent excess of lithium for 140 minutes (run 3), the organolithium compound was obtained in only 3.5 percent yield and the unreacted chloride was recovered in 50 percent yield. Prolonged reaction time has also been found to hurt both the yield and the purity of the carboxylic acid formed upon carbonation (runs 1 and 2).

In addition to the possibilities discussed earlier, there are two further side reactions which will affect the yield of the present organolithium compound; the first is the abstraction of protons from the solvent or some other source, such as impurities in the solvent, by the organolithium compound to give hydrocarbon; the second is the reduction of the desired organolithium compound by excess metal to give radical anion, e.g.



The first will cut down the yield of organolithium compound and the second will reduce both the yield and the purity of the desired organolithium compound. Increases in temperature and reaction time will both favor the first undesired side reaction; the presence of excess metal and long reac-

(46) P. Balk, G. J. Hoijtink, and J. W. H. Schreurs, Rec. trav. chim., 76, 818 (1957).

tion time will help the second side reaction.

In order to test the stability of 2-p-biphenylylethyllithium in tetrahydrofuran, the solution prepared at -73° was filtered to remove most of the excess metal and then allowed to stand at that temperature without stirring for two intervals of time (65 and 240 minutes). Carbonation gave 3-p-biphenylylpropanoic acid in 26 and 20 percent yields, respectively (run 5). In another run (run 6), the filtered solution of organolithium compound was allowed to warm to 0° and then stand at 0° ± 3° without stirring for one hour before carbonation. This experiment produced 38 percent of carboxylic acid of which 90 percent was volatile 3-p-biphenylylpropanoic acid. Thus 2-p-biphenylylethyllithium has been synthesized in tetrahydrofuran at -70° using a large excess lithium metal but short reaction time and this organolithium compound has been found to be moderately stable even at 0° in the absence of a large excess of metal.

The synthesis of 2-p-biphenylylethyllithium-2,2-d_2 in tetrahydrofuran from the reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with lithium metal is summarized in Table 14. The reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with lithium metal in tetrahydrofuran at -70° gave, upon carbonation, 69 percent of a carboxylic acid. The metling point (146-50°) showed that this acid was possibly 3-p-biphenylylpropanoic acid-d_2 contaminated by traces of impurities since pure 3-p-biphenylylpropanoic acid melts at 151°. The above acidic product was converted into methyl ester and this ester, after distillation, was analyzed by nmr. This analysis showed that it was pure methyl 3-p-biphenylylpropanoate-2,2-d_2, within experimental error (5 percent). In another run, the organolithium compound prepared at -68° was filtered and then allowed to stand at 0° ± 3° for 170 minutes

Table 14. Reaction of 1-Chloro-2-p-biphenylylethane-1,1-d_2 with Lithium

Run No.		1	2	3	4	5
RCl	g (mole)	5.01 (0.0221)	4.66 (0.0213)	4.51 (0.0206)	5.02 (0.0229)	2.01 (0.00918)
Lithium	g (g atom)	2.17 (0.313)	2.18 (0.314)	2.20 (0.317)	2.54 (0.366)	0.960 (0.138)
TMEDA	g (mole)	None	None	None	None	3.94 (0.0340)
Reaction Temperature		-70°	-68°	-73°	-71°	-65°
Time of Addition	min	17	15	15	20	25
Time of Stirring at Rxn. Temperature	min	16	15	11	3	10
Time of Standing at 0 ± 3°		None	170 min	16.5 hrs	9 hrs	1 hr
Yield of Crude Acid	g (%)	3.51 (69.3)	2.22 (45.6)	0.842 (17.9)	0.915 (17.5)	0.278 (13.3)
m.p. of Crude Acid		146-50°	137-46°	semi-solid	semi-solid	140-50°
Yield of Crude Neut. Products	g	2.41	2.52	3.45	3.83	1.74
VPC of Crude Neutral:						
p-Biphenylylethane	area %	94.0	98.6	not determined	96.0	97.0
Other Volatile Compounds		Three others	Two others		Four others	Two others

before carbonation. A 46 percent yield of carboxylic acid resulted and a small portion of it was converted into methyl ester and then purified by vacuum sublimation. The nmr of this ester showed that it was predominantly unrearranged product, methyl 3-p-biphenylylpropanoate-2,2-d_2 without rearranged ester within experimental error. When the filtered solution of a similar organolithium compound (run 4) was allowed to stand at 0° for nine hours, the yield of acidic product decreased tremendously (to 17.5 percent). A portion of this acidic product was converted into methyl ester and this ester was vacuum sublimed twice. VPC of this sublimate showed the presence of four compounds of which methyl 3-p-biphenylylpropanoate-d_2 constituted 66 percent. Further purification by recrystallization gave a sample which, according to the nmr spectrum, was methyl 3-p-biphenylylpropanoate-2,2-d_2 within experimental error. The neutral product was analyzed by VPC and found to contain, in the volatile fraction, 96 percent relative yield of p-biphenylylethane; after sublimation and recrystallization it gave 52 percent absolute yield of p-biphenylylethane. The nmr spectrum of this purified sample showed that it was 95 percent unrearranged p-biphenylylethane-2,2-d_2 and ca. 5 percent of rearranged p-biphenylylethane-1,1-d_2. In another reaction (run 3), the filtered organolithium compound prepared at -71° was allowed to warm to 0° and stand at 0° without stirring for 16 hours and 30 minutes before carbonation. This reaction gave mainly neutral product (the acidic material which was obtained in an 18 percent overall yield was found, according to VPC of the diazomethane reaction product, to contain six parts of p-biphenylylethane and one part of methyl esters). The neutral material was further purified and analyzed by both VPC and nmr and found to contain 93 percent unrearranged hydrocarbon and ca. 7 percent

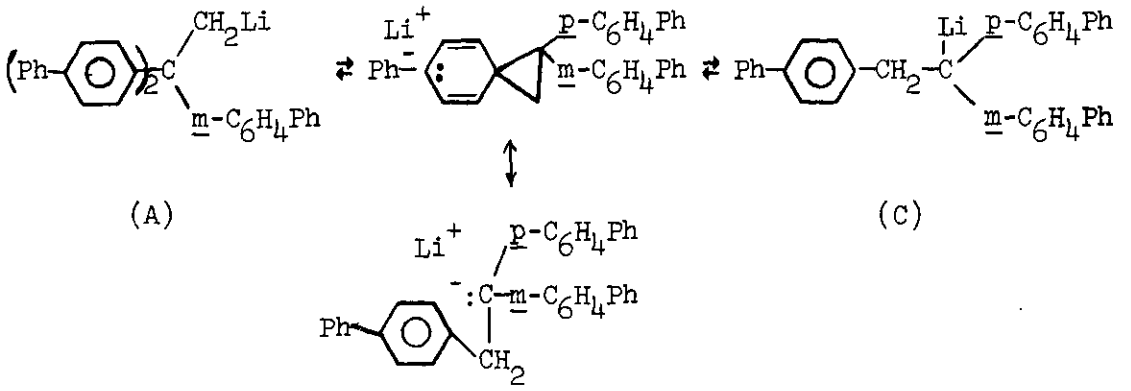
rearranged product.

An attempt was made to effect the rearrangement of 2-p-biphenylylethyllithium-1,1-d_2 by TMEDA. The reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with lithium in tetrahydrofuran was carried out at -65° in the presence of ca. four equivalents of TMEDA. After removing most of the unreacted lithium, the solution was allowed to stand at 4° for one hour with occasional shaking by hand before carbonation (run 5). The acidic product obtained in 13 percent yield was converted into methyl ester and this methyl ester was sublimed twice. The nmr spectrum of this purified methyl ester showed that it was mainly unrearranged methyl 3-p-biphenylylpropanoate-2,2-d_2 and there was no rearranged ester within experimental error (5 percent). The corresponding hydrocarbon, biphenylylethane-d_2, which was obtained in 37 percent absolute yield (by VPC), was found, after purification, to be predominantly unrearranged p-biphenylylethane-2,2-d_2 contaminated by less than 7.1 percent (if at all) of p-biphenylylethane-1,1-d_2.

Thus both 2-p-biphenylylethyllithium and 2-p-biphenylylethyllithium-1,1-d_2 are prepared in yields of over 50 percent and found to be moderately stable at -70° and at 0°. Prolonged standing at these temperatures has resulted in the protonation of part of the organolithium compounds originally prepared. The deuterium-labeled compound does not undergo rearrangement at -70° for a short time (30 minutes), and it does not give significant amount of rearrangement even at 0° for a long time (16 hours and 30 minutes). TMEDA has failed to accelerate the rearrangement of the deuterium-labeled organolithium compound under the conditions investigated.

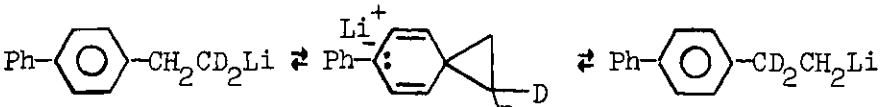
Wentworth[17] has found that 2-m-biphenylyl-2,2-bis(p-biphenylyl)

ethyllithium undergoes the following rearrangement completely at 0° in four hours.



(A) (B) (C)

Comparing the present case with his rearrangement, one would assume that the following reaction might take place:



(D) (E) (F)

The differences in the transition states (or intermediates) in these two cases are the substituents on one carbon of the cyclopropyl ring. The no-bond resonance structure contributes some to the transition state (B) and hence lowers the activation energy of his case, but the same kind of influence is not available in the present case (E). Furthermore relief of steric strain may favor Wentworth's rearrangement.

Reactions of 1-Chloro-2-p-biphenylylethane and 1-Chloro-2-p-biphenylylethane-1,1-d_2 with Cesium, Potassium, and Cs-K-Na Alloy

The reactions of 1-chloro-2-p-biphenylylethane with cesium and Cs-K-Na alloy, and potassium are summarized in Tables 15 and 16, respectively. The corresponding reactions of the deuterium-labeled halide are presented in Tables 17 and 18, respectively.

The reactions of the protium compound were run for the purpose of finding the optimum conditions for the study of the rearrangement of the corresponding deuterium compound. From three runs with the Cs-K-Na alloy (runs 1-3 in Table 15) in tetrahydrofuran at -70 ± 8°, it was revealed that the rate of addition of the halide affected the yield of the normal molecular weight products and the optimum condition was the slow addition of the halide dropwise over a period of 37 minutes to the solution of finely divided metal in the solvent. Under these conditions, p-biphenylylethane was obtained in 30 percent yield. The reaction of the same halide with cesium at 65° gave 18 percent yield of p-biphenylylethane (run 4 in Table 15). Since p-biphenylylethane was obtained in approximately 0.3 g or less, the presence of any impurity such as Nujol, which was used to store potassium, or lubricating oil, which might have been washed down from the bearing of the stirrer by the solvent, would complicate both the purification and the nmr identification of hydrocarbons of volatile products having a melting point of 32°. This difficulty was encountered in all of the cesium, potassium (discussed below), and cesium alloy reactions. The acidic products from the cesium alloy reactions were mainly high melting compounds containing less than 4 percent of any single acid of normal

Table 15. Reaction of 1-Chloro-2-p-biphenylylethane with Cesium and Cs-K-Na Alloy

Run No.		1	2	3	4
RCl	g (mole)	0.967 (0.00446)	1.01 (0.00466)	1.02 (0.00471)	2.46 (0.0114)
Cs-K-Na	g atom	0.921	0.931	0.0113	
Cs	g (g atom)				3.47 (0.0261)
Reaction Temp.		-78°	-67°	-63°	65°
Time of addition	min	3	8½	37	20
Time of stirring	min	3	1	5	5
Cooling to Room Temp.	min	not done	not done	not done	10
Yield of Crude Acid	g	0.679	1.13	0.382	not worked up
Yield of $ArCH_2CH_2CO_2H$ (by VPC)	g	0.0136	0.0018	0.00334	
Yield of Total Volatile Acids (by VPC)	g	0.0272	0.250	0.00886	
Yield of Crude Neutral Products	g	0.89	0.45	1.10	1.38
Yield of Volatile Hydrocarbons	g	0.0591	not done	0.353	0.342
VPC of Crude Neutral Products:					
$ArCH_2CH_3$		99%*	0.000327g	0.278g	0.369g (17.8%)
$ArCH{=}CH_2$		none	not determined	none	none
Low M. W. Compound(s)		1%*	0.00273g	none	4.9%*
Unreacted RCl		none	none	none	none

*Relative yields

Table 16. Reaction of 1-Chloro-2-p-biphenylylethane with Potassium

Run No.		1	2
RCl	g (mole)	1.20 (0.00553)	0.847 (0.00391)
Potassium	g (g atom)	0.478 (0.0123)	0.455 (0.0116)
t-BuOH	g (mole)	none	0.945 (0.0127)
Reaction Temperature		65°	65°
Time of Addition	min	8	5
Cooling to Room Temp.	min	10	10
Yield of Crude Acid	g	0.394	0.143
Yield of Crude Neutral Product	g	1.22	1.14
Yield of Volatile Neutral Product	g	0.554	0.550
M.P. of Volatile Neutral		oil	59-77°
VPC		only A	35% A : 62.3% B : 27% C

NOTE: A is $ArCH_2CH_3$, B is $ArCH=CH_2$, and C is an unknown compound of relative retention time 0.76 (based on A as standard).

Table 17. Reaction of 1-Chloro-2-p-biphenylylethane-1,1-d_2 with Cesium and Cs-K-Na Alloy

Run No.		1	2	3	4	5
RCl	g (mole)	0.981 (0.00448)	0.954 (0.00436)	1.53 (0.00699)	1.29 (0.00589)	2.89 (0.0132)
Cs-K-Na	g (g atom)	(0.0107)	0.827 (0.0105)	1.67 (0.0215)		
Cs					2.35 (0.0177)	4.08 (0.0307)
Reaction Temperature		-66°	-65°	-65°	36 ± 2°	65°
Time of Addition	min	40	30	30	15	31
Time of Stirring	min	5	5	5	1	10
Cooling to Room Temp.	min	none	none	none	none	10
Yield of Crude Acid	g	0.202	0.107	0.952	1.17	1.65
Yield of $ArCH_2CD_2CO_2Me$*	g	0.00119	no VPC analysis of esters	none	0.00614	none
Yield of Total Volatile Esters	g	0.00905		0.0153	0.164	0.194
Yield of Crude Neutral Products	g	1.33	1.10	0.805	0.329	1.42
Yield of Volatile Hydrocarbon(s)	g	0.261	0.254	0.291	0.0698	0.590
VPC of Crude Neutral Products:						
Ethyl biphenyl-d_2	g (%)	0.230 (27.8)	0.167 (20.8)	0.317 (24.6)	0.0601	0.470 (19.4)
Vinyl biphenyl-d_2	g (%)	0.0238 (2.91)	0.0295 (3.71)	none	none	none

Table 18. Reaction of 1-Chloro-2-p-biphenylylethane-1,1-d_2 with Potassium

Run No.		1	2	3
RCl	g (mole)	1.14 (0.0052)	0.616 (0.00281)	1.51 (0.00689)
Potassium	g (g atom)	0.449 (0.0115)	0.411 (0.0105)	0.750 (0.0192)
t-BuOD	g (mole)	none	1.59 (0.0212)	1.60 (0.021)
Reaction Temperature		65°	65°	65°
Time of Addition	min	5	immediately	15
Time of Stirring	min	5	5	5
Cooling to Room Temp.	min	10	none	5
Yield of Crude Acid	g	0.34	no work-up	0.048
Yield of Crude Neutral	g	1.16	0.860	1.40
VPC of Crude Neutral		only A	6.2% A, 79.2% B, 11.9% C, 2.0% of three others	39.1% A 52.9% B 8.0% C

NOTE: A is $ArCH_2CD_2H$, or $ArCD_2CH_3$, $ArCH_2CD_3$, $ArCD_2CH_2D$, etc.
B is $ArCH{=}CD_2$
C is unknown of relative retention time 0.75

molecular weight and 3-p-biphenylylpropanoic acid was obtained in less than 1.3 percent absolute yield. The reaction of potassium with the protium compound in refluxing tetrahydrofruan gave mainly neutral product which contained 40 percent of volatile material (run 1 in Table 16). VPC showed that this volatile product was mainly p-biphenylylethane. However, the nmr spectrum of a sublimate indicated that the p-biphenylylethane isolated was contaminated by the impurities mentioned above. The acidic product from this potassium reaction was converted into methyl ester and VPC of this methyl ester yielded 4.9 percent (absolute yield) of a compound, which after purification was analyzed by nmr and found to be methyl 2-p-biphenylylpropanoate contaminated by impurities possibly from the lubricant of the bearing. The reaction of potassium with a mixture of the same chloride and t-BuOH gave, upon carbonation, mainly neutral material, which after three sublimations yielded 70 percent (absolute yield) of a crystalline material. This crystalline product was found by VPC to contain 35 percent p-biphenylylethane, 62.3 percent p-biphenylylethene, and 2.7 percent (all relative yields) of an unknown compound of relative retention time 0.76 (based on p-biphenylylethane as standard). One recrystallization from ethanol gave a crystalline material containing 85 percent of the olefin and 15 percent of p-biphenylylethane.

The reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with slight excess of Cs-K-Na alloy in tetrahydrofuran at -65° (runs 1 and 2 in Table 17) gave, upon carbonation, mainly neutral material which yielded 2.8 percent of p-biphenylylethane-d_2 and 3.0 percent of p-biphenylylethene along with 10 percent unreacted chloride (all in absolute yields). The purification and analysis of p-biphenylylethane-d_2 in order to determine the extent

of rearrangement failed because of the incompletion of the reaction and the presence of impurities especially lubricating oil which interfered in the methyl group region of the nmr spectrum of the hydrocarbons. In another run (run 3), the chloride was reacted with a thoroughly washed alloy in tetrahydrofuran at -65° by adding a tetrahydrofuran solution of the chloride to a blue solution of cesium alloy in tetrahydrofuran. Then the resulting black-brown solution was stirred at that temperature for five minutes and finally carbonated. This reaction yielded approximately a 1:1 mixture of acidic and neutral products. The volatile methyl esters of the acidic material were found to give less than 1 percent overall yield of six compounds, none of which was identified as 3-p-biphenylylpropanoic acid by VPC of their methyl esters. The neutral product yielded, according to VPC, 25 percent (absolute yield) of p-biphenylylethane-d_2 as the only volatile hydrocarbon. After purification this hydrocarbon was analyzed by nmr and found to contain 77.7 percent of p-biphenylylethane-2,2-d_2 (I) and 22.3 percent of p-biphenylylethane-1,1-d_2 (II).

The same chloride reacted with cesium metal in refluxing tetrahydrofuran to give, upon carbonation, again approximately a 1:1 ratio of acidic and neutral products. The neutral product was found to yield 19 percent (absolute yield) of p-biphenylylethane-d_2 together with some 5 percent of an impurity of lower retention time which was identified as p-biphenylylmethane by VPC. p-Biphenylylethane-d_2 was purified and then analyzed by nmr and found to contain 47.9 percent of p-biphenylylethane-2,2-d_2 (I) and 52.1 percent of p-biphenylylethane-1,1-d_2 (II). A mass spectrum of this sample showed 94 percent d_2, 3.6 percent d_1, and 2.4 percent d_3 compounds. Thus it was mainly (I) and (II). The d_3 and d_1 compounds were possibly

p-$PhC_6H_4CD_2CH_2D$ or p-$PhC_6H_4CH_2CD_3$, and p-$PhC_6H_4CHDCH_3$, respectively. The formation of the d_1 and d_3 compounds may be explained by the following reactions:

$$ArCD_2CH_3 \xrightarrow{ArCH_2CD_2^-} ArCH_2CD_3 + Ar\underline{C}DCH_3 \xrightarrow{H^+} ArCHDCH_3$$

$$\xrightarrow{ArCD_2CH_2^-} ArCD_2CH_2D + Ar\underline{C}DCH_3 \xrightarrow{H^+} ArCHDCH_3$$

$$ArCD_2CH_3 \xrightarrow{Cs} Ar\underline{C}DCH_3 \xrightarrow{H^+} ArCDHCH_3$$

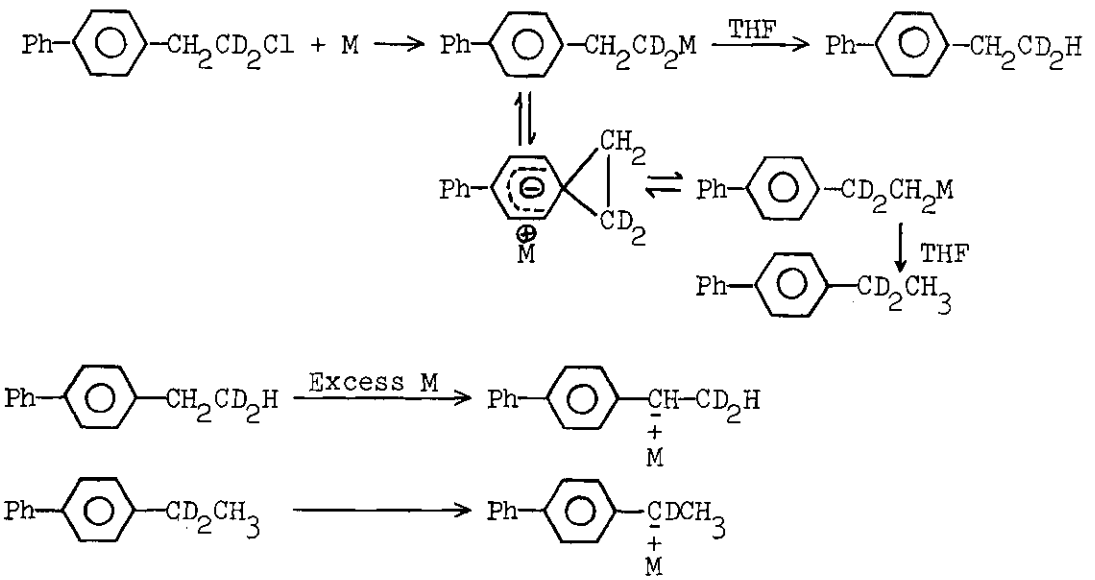
The starting chloride was found to be at least 99 percent pure in 1-chloro-2-p-biphenylylethane-d_2 by mass spectroscopic analysis. The acidic product was converted into methyl esters and then analyzed by VPC to yield 6.0 percent (absolute yield) of an ester (identified by nmr as methyl 2-p-biphenylylpropanoate-3,3-d_2 of relative retention time 0.75) along with some 0.15 percent of an impurity of shorter retention time.

An attempt to react the same chloride with cesium at 36° resulted in the formation of low absolute yields of volatile products (ca. 6 percent p-biphenylylethane-d_2 and 14 percent volatile acids which contained less than 6 percent of 3-p-biphenylylpropanoic acid), which made the purification and further identification of the products complicated.

The reaction of this deuterium-labeled chloride with potassium in refluxing tetrahydrofuran (run 1 in Table 18) gave upon carbonation mainly

neutral material. This neutral product yielded, after one sublimation, 61 percent absolute yield of p-biphenylylethane-d_2 which was sublimed a second time, recrystallized, and then analyzed by nmr and found to contain 47.1 percent of p-biphenylylethane-2,2-d_2 (I) and 52.9 percent of p-biphenylylethane-1,1-d_2 (II).

A blank test has shown that, under the conditions of potassium and cesium reactions, 1-chloro-2-p-biphenylylethane-1,1-d_2 itself does not undergo rearrangement. Thus, contrary to the lithium compound, both 2-p-biphenylylethylcesium and/or 2-p-biphenylylethylpotassium undergo partial (ca. 45 percent) rearrangement before protonation in tetrahydrofuran at -65°; both cesium and potassium compounds undergo complete rearrangement in refluxing tetrahydrofuran. The slight excess of (II) over (I) in the product distribution is apparently due to an isotope effect which makes (I) preferentially matalated on the α-carbon by excess metal.

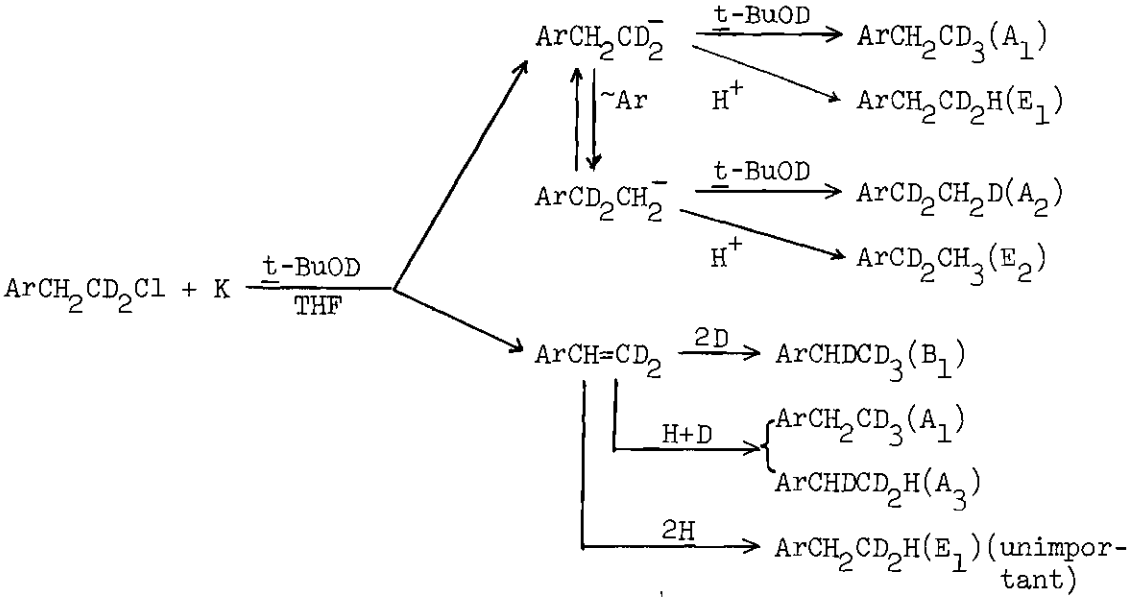


Efforts were made to trap 2-p-biphenylylethyl-d_2 anion before rearrangement by reacting a mixture of the chloride and t-BuOD with potassium in refluxing tetrahydrofuran. In the first run, potassium after stirring in tetrahydrofuran, was allowed to agglomerate and then reacted with the mixture of the chloride and t-BuOD. This reaction resulted in the formation of a mixture containing 79 percent p-biphenylylethene-d_2 and 6 percent p-biphenylylethane-d_2 and four unknown products. The determination of the amount of rearrangement by the analysis of p-biphenylylethane-d_2 was unsuccessful because of its low content in the mixture; however, the corresponding olefin was found to contain no significant amount of rearrangement (nmr analysis). The reaction was repeated by adding a mixture of the chloride and t-BuOD dropwise to a solution of potassium in refluxing tetrahydrofuran under vigorous stirring. Upon carbonation, there was obtained a mixture containing 39.1 percent p-biphenylylethane (A), 52.9 percent of p-biphenylylethene (B), together with some 8.0 percent of a shorter retention time compound (C). After sublimation and recrystallization, a fraction which contained only (A) and (B) in a ratio of 1.07 : 1.00 was analyzed by both nmr and mass spectrometer. The nmr spectrum indicated a ratio (5.2) of methylene protons to methyl protons. The mass spectrum [mass (abundance): 184 (15.9 percent), 185 (49.8 percent), 186 (29.1 percent), 187 (4.2 percent), and 188 (1.0 percent)] indicated that the compound (A) contains not only d_3 compounds but also d_2, d_4, and d_5 compounds. The mass, abundance, possible compounds, and their designations are given in Table 19.

Table 19. The Mass, Abundance (after correction for C-13), Possible Compounds, and Designation of the Saturated Hydrocarbon Products

Mass	Abundance %	Possible Compound (designation)
184	15.9	$ArCH_2CD_2H(E_1)$, $ArCD_2CH_3(E_2)$, $ArCHDCH_2D(E_3)$
185	49.8	$ArCH_2CD_3(A_1)$, $ArCD_2CH_2D(A_2)$, $ArCHDCD_2H(A_3)$
186	29.1	$ArCHDCD_3(B_1)$, $ArCD_2CHD_2(B_2)$
187	4.2	$ArCD_2CD_3(C)$
188	1.0	$C_{12}H_8DCD_2CD_3(D)$

In Table 19, E_1, A_1, A_3, B_1, B_2, C, and D correspond to unrearranged skeleton, and E_2 and A_2 correspond to rearranged skeleton. The sources of the compounds listed in Table 19 are summarized in the following equations:



$$(E_1) \xrightarrow{\text{D exchange}} ArCHDCD_2H(A_3) \xrightarrow{\text{D exchange}} ArCD_2CD_2H(B_2)$$

$$(A_1) \xrightarrow{\text{D exchange}} ArCHDCD_3(B_1) \xrightarrow{\text{D exchange}} ArCD_2CD_3(C)$$

(E_3) could possibly form from proton exchange of (A_2), since A_2 is small, (E_3) is even smaller and for a first approximation, (E_3) can be neglected.

From the calculation given in Appendix C, it was found, according to nmr and mass spectra, that the reaction of 1-chloro-2-p-biphenylylethane-1,1-d_2 with potassium and t-BuOD in refluxing tetrahydrofuran gave besides olefin, some 39 percent of saturated hydrocarbons. One half of these saturated hydrocarbons were d_3 compounds containing mainly (> 90 percent) unrearranged compound which formed predominantly (> 90 percent) from the carbanion, 2-p-biphenylylethylpotassium, with t-BuOD (the reduction of olefin is insignificant). The accompanied d_2 compounds presumably resulted from the protonation of the corresponding carbanions by tetrahydrofuran or other proton source. The presence of both d_4 and d_5 compounds in significant proportions strongly suggested that deuterium exchange took place at α-carbons of the saturated hydrocarbon products. The olefin was found to be predominantly $ArCH{=}CD_2$ by nmr and mass spectral analyses.

In summary, it is concluded that the reaction of 1-chloro-2-p-biphenyl-1,1-d_2 with both cesium and potassium in refluxing tetrahydrofuran gives first a carbanion which undergoes rearrangement, conceivably through a bridged transition state (or intermediate), to yield a 1:1 equilibrium mixture of both rearranged and unrearranged carbanions. These carbanions are short-lived under reaction conditions because of fast protonation by

the solvent. If the solvent contains t-butyl alcohol most of the carbanions are protonated before rearrangement can occur. If the reaction is run at -65° with a ternary Cs-K-Na alloy, only 44 percent rearrangement occurs before protonation by solvent. On the contrary, the corresponding organolithium compound does not undergo rearrangement to any significant extent. This difference could possibly be due to the fact that the organocesium and -potassium compounds exist as fairly loose ion pairs while the lithium compound exists as an intimately bound tetramer, each 2-p-biphenylylethyl group being tightly bound to three lithium atoms.

CHAPTER VI

RECOMMENDATIONS

The synthesis of simple primary carbanions has not been extensively studied in the solvent trimethylamine; this may prove to be a good solvent if manipulated with special care. The success in the syntheses of β-arylethyllithium compounds with two β-hydrogens may serve as a pioneer in the studies of rearrangements of analogous systems like ring substituted β-arylethyllithium. It would also be interesting to extend the number of aliphatic carbons and thus to study the syntheses and rearrangements of ω-arylalkyl carbanions, such as 4-arylbutyl anion.

The possibility of using a polyether like Crown Ether[47] as a chelating agent to activate and promote the rearrangement of an organoalkali compound is also an interesting topic for study.

Study of the extent of phenyl migration during reaction of neophyl bromide with lithium may be of interest for comparison with the present work upon neophyl chloride. The photochemistry of neophyllithium in the presence of photosensitizer may also be an interesting problem.

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(47) C. J. Pederson, J. Am. Chem. Soc., 92, 386 (1970); C. J. Pederson, ibid., 92, 391 (1970); C. J. Pederson, ibid., 89, 7017 (1967).

APPENDIX A

INFRARED SPECTRA OF p-BIPHENYLYLETHYL AND p-BIPHENYLYLETHYL-d_2 COMPOUNDS

The infrared spectral data of 2-p-biphenylylethanol, 2-p-biphenylylethanol-1,1-d_2, 1-chloro-2-p-biphenylylethane, and 1-chloro-2-p-biphenylylethane-1,1-d_2 are listed in Table 20.

Table 20. Infrared Spectral Data*

Compound	Bands in (μ) and Intensity in Parentheses
p-$PhC_6H_4CH_2CH_2OH$	2.77(m), 2.91(m), 3.25(m), 3.29(m), 3.30(s), 3.41(s), 3.42(s), 3.48(m), 4.43(w), 5.14, 5.17, 5.30, 5.39, 5.68, 5.79(all w), 6.77(s), 6.82, 6.99, 7.16, 7.28, 7.59(all w), 9.12(w), 9.38(m), 9.61(s), 10.0(m)
p-$PhC_6H_4CH_2CD_2OH$	2.78(m), 2.92(w), 3.26, 3.29(all m), 3.31(s), 3.34(w), 3.41(m), 3.45(m), 3.54(w), 4.41(w), 4.55(m), 4.77(m,C-D stretching), 5.17, 5.27, 5.37, 5.66(all w), 6.75(s), 6.80, 6.96, 7.14, 7.69(all w), 9.00, 9.12, 9.34(all m), 9.94(s), 10.0, 10.4 (all m).
p-$PhC_6H_4CH_2CH_2Cl$	3.23, 3.25, 3.28, 3.32, 3.37(all s), 3.43, 3.48 (all m), 5.17, 5.28, 5.36, 5.59, 5.79, 6.10 (all w), 6.27, 6.74, 6.92, 6.97, 7.12(all s), 7.60(m), 7.75(s), 8.04(m), 8.82(w), 9.14(m), 9.31, 9.88, 10.3(all m), 11.2(s).
p-$PhC_6H_4CH_2CD_2Cl$	3.20(w), 3.23, 3.26, 3.27(all s), 3.40, 3.43, 3.49 (all m), 3.50(w), 4.48(w), 4.64(m, C-D stretching), 5.01, 5.16(all w), 5.28(m), 5.35(w), 5.59(m), 5.75 (w), 6.05(w), 6.25, 6.72, 6.92 (all s), 6.97(m), 7.10(s), 8.37(m), 9.02(s), 9.14(m), 9.77, 9.87 (all s), 10.2(m), 11.1(w).

*Carbon tetrachloride was used as solvent; the alcohols are not very soluble in this solvent.

APPENDIX B

ANALYSIS OF $LiAlD_4$

The aluminum content of $LiAlD_4$ (see Chapter II) used for reductions was determined according to a standard method.[48]

Two aliquots of $LiAlD_4$/tetrahydrofuran solution were filtered quickly through glass wool in a small Buchner funnel covered with aluminum foil and then hydrolyzed with water. The filtrate was dried on a hot plate and the residue was dissolved in about 1 N HCl. To this solution was added one drop of methyl red solution and a 10 percent excess of 0.1 N ethylenediamine tetracetic acid (EDTA) solution; the resulting solution was neutralized to yellow with a solution of NH_4OH containing 1:1 ratio (by volume) of NH_4OH and water. Then the solution was boiled for two minutes, allowed to cool to room temperature, and then 20 ml of pH 4 buffer (ammonium acetate-acetic acid) was added. Enough ethanol was added to make final volume of sample 40 percent ethanol. Dithizone indicator (2 ml) was added for each 100 ml of solution; a few ml of HOAc was added to bring to a blue-green color. The resulting solution was titrated with $Zn(OAc)_2$ to a pink color. The content of aluminum was calculated by the following equation:

$$\text{Grams of Al} = (N_{EDTA} \times ml_{EDTA} - N_{Zn(OAc)_2} \times ml_{Zn(OAc)_2}) \times 0.027$$

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(48) G. Schwarzenbach and H. F. Flaschka, "Complexometric Titrations," Methuen & Co. Ltd., New York, 1969, p. 192 (translated by H. M. N. H. Irving).

APPENDIX C

CALCULATION FOR THE PRODUCTS FROM POTASSIUM-t-BuOD REACTION

As discussed in Chapter V (page 129), the reaction of 1-chloro-2-p-biphenylylethane with potassium and t-BuOD gave, besides olefin, some 39 percent relative yield of p-biphenylylethane consisting of 15.9 percent d_2, 49.8 percent d_3, 29.1 percent d_4, 4.2 percent d_5, and 1.0 percent d_6 compounds. The d_2 compounds could be $ArCH_2CD_2H(E_1)$, $ArCD_2CH_3(E_2)$, or $ArCHDCH_2D(E_3)$(negligible); the d_3 compounds could be $ArCH_2CD_3(A_1)$, $ArCD_2CH_2D(A_2)$, or $ArCHDCD_2H(A_3)$; the d_4 compounds could be $ArCHDCD_3(B_1)$, $ArCD_2CD_2H(B_2)$; the d_5 compound could be $ArCD_2CD_3(C)$; the d_6 compound could be $C_{12}H_8DCD_2CD_3(D)$(see Table 19 on page 130). The possible sources of these compounds are given on page 130.

If one assumes that there is no reduction of $ArCH{=}CD_2$, no hydrogen from solvent replacing deuterium in ArEt via exchange, one can set up an equation:

$$\frac{2E_1 + 2A_1 + A_3 + B_1}{E_1 + 2A_2 + 3E_2 + B_2 + A_3} = K = 5.2 \qquad (1)$$

where A_1, A_2. . . etc. are relative molecular abundances of each component listed in Table 19 and 5.2 is the observed ratio of α-H's to β-H's by nmr. For simplicity, one may assume that A_3 is negligible relative to A_1 and hence also B_2 is negligible, thus,

$$E_1 + E_2 = 15.9\% \quad (2)$$

$$A_1 + A_2 = 49.8\% \quad (3)$$

$$B_1 = 29.1\% \quad (4)$$

$$C = 4.2\% \quad (5)$$

In the following reactions with deuterium and proton donors, SD and SH:

$$ArCH_2CD_2\cdot \;(F) \xrightarrow{k_{A_1}} ArCH_2CD_3$$

$$ArCH_2CD_2\cdot \;(F) \xrightarrow{k_{E_1}} ArCH_2CD_2H$$

$$ArCD_2CH_2\cdot \;(G) \xrightarrow{k_{A_2}} ArCD_2CH_2D$$

$$ArCD_2CH_2\cdot \;(G) \xrightarrow{k_{E_2}} ArCD_2CH_3$$

$$\frac{k_{A_1}}{k_{E_1}} = \frac{k_{A_2}}{k_{E_2}}$$ true within error of secondary isotope effects

$$\frac{k_{A_1}(SD)(F)}{k_{E_1}(SH)(F)} = \frac{k_{A_2}(SD)(G)}{k_{E_2}(SH)(G)} = \frac{d(A_1)}{d(E_1)} = \frac{d(A_2)}{d(E_2)} = \frac{k_{A_1}(SD)}{k_{E_1}(SH)} = k$$

if (SD)/(SH) is constant or effectively so per drop of addition. The above differential equation is of the type

$$\frac{dx}{dy} = k \quad \text{or}$$

$$x = ky + c \quad \text{but}$$

at t = 0, x and y = 0 $\quad\therefore\ c = 0,$ or

$$x = ky$$

Hence

$$(A_1) = k(E_1) \qquad (A_2) = k(E_2) \qquad \therefore \quad \frac{(A_1)}{(A_2)} = \frac{(E_1)}{(E_2)}$$

Let

$$\frac{(E_1)}{(E_2)} = \frac{(A_1)}{(A_2)} = \alpha$$

From equations (2) and (3), one finds that

$$E_1 = \left(\frac{\alpha}{1+\alpha}\right) \times 15.9 \qquad A_1 = \left(\frac{\alpha}{1+\alpha}\right) \times 49.8$$

$$E_2 = \left(\frac{1}{1+\alpha}\right) \times 15.9 \qquad A_2 = \left(\frac{1}{1+\alpha}\right) \times 49.8$$

Substituting these and (B_1) into equation (1) above,

$$\frac{2 \times 15.9 \left(\frac{\alpha}{1+\alpha}\right) + 2 \times 49.8 \left(\frac{\alpha}{1+\alpha}\right) + 0 + 29.1}{15.9 \left(\frac{\alpha}{1+\alpha}\right) + 3 \times 15.9 \left(\frac{1}{1+\alpha}\right) + 2 \times 49.8 \left(\frac{1}{1+\alpha}\right) + 0 + 0} = 5.2$$

one obtains $\quad \alpha = 9.47$

Thus, the maximum yield of rearrangement is

$$\frac{1}{1 + 9.47} \times 100 = \frac{1}{10.47} \times 100 = 9.55\%$$

If, on the contrary, one assumes that (1) no rearrangement and no reduction of styrene; (2) the secondary isotope effect is negligible in

the deuterium exchange reactions; (3) A_3 and B_1 are so small that negligible reversal back to E_1 and A_1 occurs; this would be true if percent exchange is small or if concentration of S-H is small; (4) the second exchange of D for H in ethylbenzene is negligibly small, i.e., the concentrations of B_2 and C are negligibly small (this is indeed observed to be the case for C which is only 4.2 percent abundance and undoubtedly B_2 is even smaller), then for the following exchange reactions a simple relationship can be derived.

$$\underset{E_1}{ArCH_2CD_2H} \underset{k_{-E_1}}{\overset{k_{E_1}}{\rightleftharpoons}} \underset{-}{ArCHCD_2H} \xrightarrow[SD]{k} \underset{A_3}{ArCHDCD_2H}$$

$$\underset{A_1}{ArCH_2CD_3} \underset{k_{-E_1}}{\overset{k_{E_1}}{\rightleftharpoons}} \underset{-}{ArCHCD_3} \xrightarrow[SD]{k} \underset{B_1}{ArCHDCD_3}$$

$$\frac{d(A_3)}{dt} = \text{net rate} = k_{E_1}(E_1)(B:)\,\frac{k(SD)}{k(SD) + k_{-E_1}(SH)}$$

$$\frac{d(B_1)}{dt} = k_{E_1}(A_1)(B:)\,\frac{k(SD)}{k(SD) + k_{-E_1}(SH)}$$

$$\frac{d(A_3)}{d(B_1)} = \frac{(E_1)}{(A_1)}$$

$$\frac{d(A_3)}{d(B_1)} = \frac{(E_1)_o - (A_3)}{(A_1)_o - (B_1)} \; ; \; \frac{d(A_3)}{(E_1)_o - (A_3)} = \frac{d(B_1)}{(A_1)_o - (B_1)}$$

$$-\ln[(E_1)_o - (A_3)] = -\ln[(A_1)_o - (B_1)] + C$$

At time ($t = 0$), when $(E_1) = (E_1)_o$ and $(A_1) = (A_1)_o$

$$C = -\ln(E_1)_o + \ln(A_1)_o$$

$$\therefore \quad -\ln[(E_1)_o - (A_3)] = -\ln[(A_1)_o - (B_1)] - \ln(E_1)_o + \ln(A_1)_o$$

$$\ln\left[\frac{(E_1)_o}{(E_1)_o - (A_3)}\right] = \ln\left[\frac{(A_1)_o}{(A_1)_o - (B_1)}\right]$$

$$\therefore \quad \frac{(E_1)_o}{(E_1)_o - (A_3)} = \frac{(A_1)_o}{(A_1)_o - (B_1)}$$

$$\therefore \quad \frac{(E_1)_o}{(A_1)_o} = \frac{(E_1)_o - (A_3)}{(A_1)_o - (B_1)} = \frac{(E_1)}{(A_1)} = \beta$$

The above equation shows that $(E_1)/(A_1)$ is constant at all times as far as their loss via D-exchange is concerned. This equation should hold (a) if the total exchange period is greater than the total formation period of E_1 and A_1, or (b) if for each drop of β-arylethyl chloride added, the exchange period is greater than the reduction period of halide within the drop.

From the same equation it can be shown that

$$\frac{(A_3)}{(B_1)} = \beta$$

Hence

$$\frac{(E_1)}{(A_1)} = \frac{(A_3)}{(B_1)} = \frac{15.9}{(A_1)} = \frac{49.8 - (A_1)}{29.1}$$

$$(A_1) = 37.4 \text{ and } (A_3) = 49.8 - (A_1) = 12.4$$

Substituting these data all of which are derived only from mass spectrum into equation (1),

$$\frac{2 \times 15.9 + 2 \times 37.4 + 12.4 + 29.1}{15.9 + 0 + 0 + 0 + 12.4} = K = 5.23$$

one obtains a value of K of 5.23 which is identical to the value obtained independently from the nmr data.

The conclusion from both calculations is, therefore, that little, if any, 1,2-rearrangement of aryl occurs and also that little, if any, p-biphenylylethane is formed by reduction of p-biphenylylethene.

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VITA

Yao-Ming Cheng was born October 12, 1936, in Hsin-Chu, Taiwan, Republic of China. From 1936, he resided in Hsin-Chu, Taiwan, and attended primary and junior high schools until his graduation from Taiwan Provincial Hsin Chu Industrial Vocational School in July, 1953 in chemical engineering. He entered Taiwan Provincial Taipei Institute of Technology (Five-Year Division) in September of 1953 and graduated with a B.S. Equivalent in Chemical Engineering in July of 1958. In August of 1958, he entered the Chinese Army and was trained as an ordnance officer; then he was assigned to the Chinese Marine Corps as a Second Lieutenant, Arm and Ammunition Officer, until his release in 1960. From July of 1960 until September of 1963, he worked with the Union Industrial Research Institute of the Ministry of Economic Affairs of Republic of China, Hsin-Chu, Taiwan. He came to the United States and entered the graduate school of the Georgia Institute of Technology in September of 1963, completing requirements for the degree Master of Science in Chemistry in January, 1967, and for the degree Doctor of Philosophy in chemistry in September 1970. From July of 1966 until June of 1967, he worked as graduate research assistant for the Engineering Experiment Station, Georgia Institute of Technology. He is a member of the Society of the Sigma Xi and the American Chemical Society.

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